ON THE THEORY OF NEMATICS

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PROMOTOR: PROF.DR. G. VERTOGEN

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VOORWOORD

Iedereen die aan het tot stand komen van dit proefschrift heeft bijgedragen: heel hartelijk bedankt.

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Tenslotte ben ik Dr. F. Leenhouts erkentelijk voor zijn bijdrage tot hoofdstuk VI.

The word nematics on the cover of this thesis is composed of spherocylinders in honour of Lars Onsager for his contribution to the microscopic theory of nematics.

To all animals,
for their patience with human beings.

CONTENTS

CHAPTER I

INTRODUCTION

This thesis deals with the nematic and the cholesteric liquid crystalline phase, the latter being a spontaneously deformed nematic phase.

In the nematic phase the centers of mass of the, usually oblong[1], constituent molecules move at random as in an isotropic liquid, while, on the average, the long molecular axes point in a certain direction. This preferred direction is denoted by an unit vector $\vec{n}$ called the director.

The cholesteric phase differs from the nematic phase in the sense that in the equilibrium situation the director $\vec{n}(\vec{r})$ rotates around a given axis, the helix axis, instead of being a constant, see Fig. I. Right-handed and left-

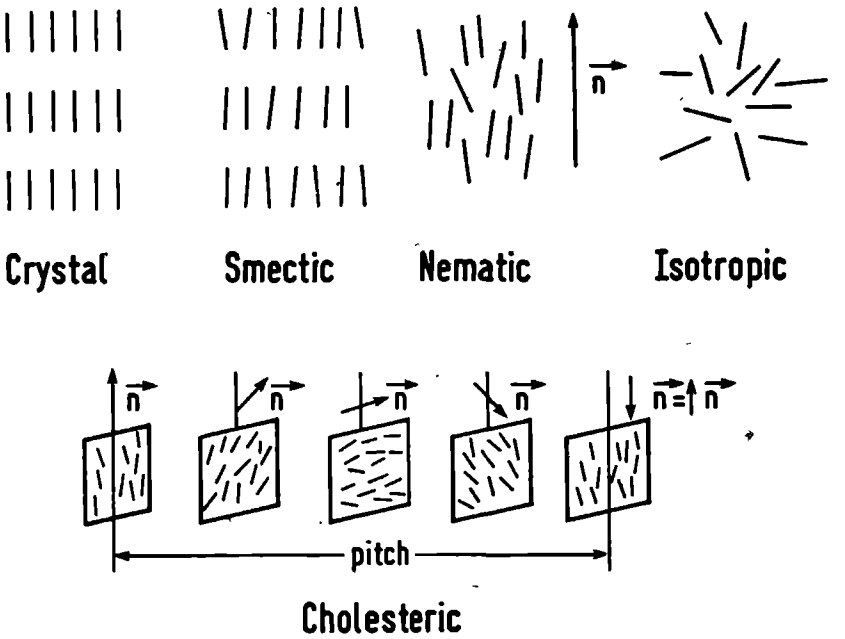
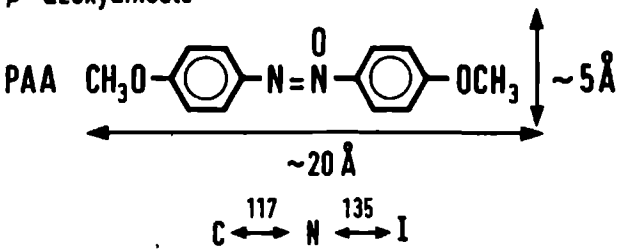
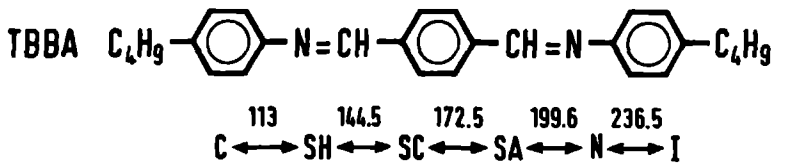


FIG. I: Schematic arrangement of molecules in a number of phases. The planes in the cholesteric phase are drawn for convenience, but do not have a physical meaning.

p-azoxyanisole



terephthalidene-bis-(4-*n*-butylanaline)



cholesteryl *p*-methoxybenzylidene-*p'*- aminobenzoate

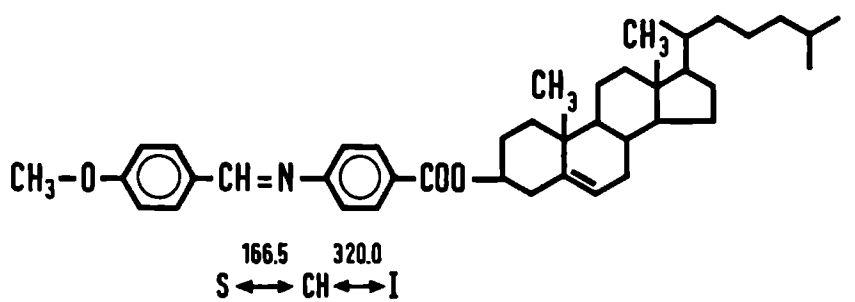


FIG. II: Examples of liquid crystals: C=crystal, N=nematic, I=isotropic, SH, SC and SA denote different smectic phases, S=solid and CH=cholesteric. The various transition temperatures, expressed in degrees Celsius, are indicated above the arrows.

handed cholesterics are distinguished, depending on the helical sense of rotation of the axis. The spatial period of the screw is called the pitch of the helical structure.

Fig. I shows, apart from the different phases mentioned before, a schematic picture of a smectic-A liquid crystalline phase. Here the molecules are arranged in equidistant layers, which slip more or less freely over each other. At present eight different types of smectics, type A up to H, are distinguished. The difference between the smectic phases and the nematic phase concerns the spatial ordering of the centers of mass of the molecules and the coupling between the spatial ordering and the orientational ordering. In the following no further attention is paid to the smectic phases[2].

Only a restricted class of organic molecules, which have in common an oblong structure together with a rigid center part, is able to form liquid crystalline phases. Some examples are given in Fig. II. The different phase-transitions are accomplished by

(a) temperature changes (thermotropic liquid crystals) as in the case of *p*-azoxyanisole (PAA) and the cholesterol esters, see Fig. II.

(b) changes of the concentration of the organic compound in an appropriate solvent (lyotropic liquid crystal); an example is tabacco mosaic virus dissolved in water.

The cholesteric phase occurs when the molecules are optically active, i.e. possess at least one asymmetric carbon atom, like e.g. the cholesterol esters. This phase can also be induced by adding optically active molecules to a nematic.

Fig. III shows two different nematic states, which give rise to the same

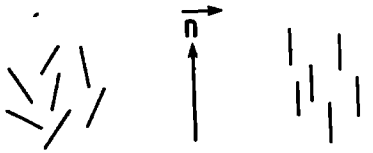


FIG. III: Two different nematic states with the same director $\vec{n}$.

$\vec{n}$. In order to discriminate between these states an order parameter, S, is introduced. This order parameter also accounts for the following experimental data

(i) the nematic phase is uniaxial, i.e. mainly the angle between the long axis of the molecule and the director $\vec{n}$ is relevant

(ii) at present no ferroelectric nematics are known, although the constituent molecules may be polar. Therefore the average orientation in the nematic phase can be indicated by both $\vec{n}$ and $-\vec{n}$.

Hence the order parameter S is defined in the following way

$$S = \sum_{i=1}^{N} \frac{\langle 3(\vec{a}_i.\vec{n})^2-1\rangle}{2N} = \frac{\langle 3(\vec{a}.\vec{n})^2-1\rangle}{2}$$

where N is the number of molecules in the system, the unit vector $\vec{a}_i$ denotes the orientation of molecule i and the brackets denote a statistical average. Remark that S = 1 corresponds with the situation that all molecules are parallel with $\vec{n}$ (perfect ordering), whereas S = 0 denotes the isotropic liquid. The behaviour of S will depend, amongst others, on the chemical structure of the molecules, the external pressure, the temperature and the particle number density. In order to give an appropriate description of S in terms of these quantities knowledge of the equation of state is essential. For this reason the next three chapters are devoted to a rather phenomenological derivation of an equation of state for nematics and the practical value of the proposed equation of state.

In chapter II a very simple straight-forward phenomenological derivation of the equation of state for nematics is presented. Here the molecules are conceived as hard rods. In the case of hard spherocylinders, i.e. cylinders which are capped by hemispheres at both ends, a quantitative comparison with existing equations of state is made.

In chapter III also attractive interactions between the molecules are taken into account in the mean field approximation. The modelcalculations are

compared with the experimental data for a number of thermotropic nematics, including two homologous series. A reasonably quantitative agreement between theory and experiment can be obtained for all nematics considered. However, a physically satisfactory description of the mutual differences between the various nematics does not appear to be possible.

Recently nematics consisting of disklike instead of rodlike molecules have been synthetized. In both cases the molecular shape can be approximately described by a cylinder, rods having a large length-to-width ratio and disks having a small lenght-to-width ratio. In chapter IV the thermodynamical behaviour of such a system of cylinders is examined. The modelresults are compared with those for spherocylinders and with the experimental data for PAA.

In the last two chapters of this thesis attention is paid to deformations in the nematic and cholesteric phases. These deformations play an important part in practical applications of liquid crystals, e.g. displays. The three basic deformations: twist, bend and splay, are sketched in Fig. IV.

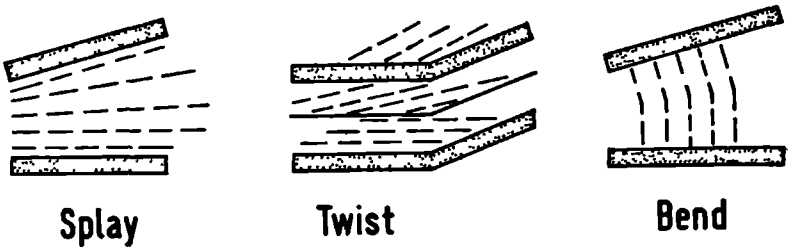


FIG. IV: The three basic deformations splay, twist and bend in the case of a nematic between two glass slides.

The increase of the free energy density in a liquid crystalline medium due to the different deformations, $f_d(\vec{r})$, can be written as follows

$$f_d(\vec{r}) = \frac{K_s}{2} (\text{div } \vec{n}(\vec{r}))^2 + \frac{K_t}{2} (\vec{n}(\vec{r}).\text{rot } \vec{n}(\vec{r}))^2$$

$$+ \frac{K_b}{2} (\vec{n}(\vec{r}) \times \text{rot } \vec{n}(\vec{r}))^2 + \frac{2\pi}{p} K_t (\vec{n}(\vec{r}).\text{rot } \vec{n}(\vec{r}))$$

where K_s, K_t and K_b denote the elastic constants for splay, twist and bend respectively and p is the natural pitch of the material ($p = \infty$ for a nematic). A simple derivation of this expression for $f_d(\vec{r})$, using tensor analysis, is given in chapter V, where also the mutual ratios of the elastic constants are calculated for a number of intermolecular interactions.

Finally the temperaturedependences of K_s, K_t and K_b, as predicted by some available molecular statistical theories, are compared with experiment in chapter VI.

References:

1 There exist nematics consisting of molecules with a disklike structure, see reference 1 of chapter IV.

2 More information about smectics and liquid crystals in general can e.g. be found in

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CHAPTER II

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ON THE HARD CORE EQUATION OF STATE FOR NEMATICS

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An equation of state is proposed for a system of rods interacting only through hard core repulsions. A quantitative comparison is made with recently proposed equations of state based upon the scaled particle and Percus–Yevick theory

Recently Cotter [1] (C) and Ypma and Vertogen [2] (YV) proposed an equation of state for nematics Cotter's derivation is rather unsatisfactory from the molecular statistical point of view because it relies on an assumed expression for the reversible work of adding a scaled spherocylinder to the fluid and does not give a unique way to obtain thermodynamic consistency Besides the derived equation of state only gives a qualitative description of the behaviour of nematics. YV took a different point of view Because the density of a nematic is that of a normal liquid, they looked upon a nematic as a normal fluid and treated its anisotropic properties in terms of perturbation theory Although the resulting equation of state gives a good description of a nematic like *p*-azoxyanisole (PAA), it is no more satisfactory because the actual length-to-breadth ratio of the molecule is abandoned and replaced by a parameter Concluding till now, a satisfactory molecular statistical derivation of the equation of state for nematic liquid crystals has not been given nor does even a satisfactory equation of state exist This conclusion also holds partly for a "simple" system of hard spheres. In the latter case, however, many satisfactory equations of state are available, notably those based upon the Percus–Yevick [3] and the scaled-particle theories [4]

The purpose of this paper is to propose an equation of state for hard rods by an appropriate generalization of the equation of state for hard spheres and further to compare it with existing equations of state This phenomenological approach appears to yield a number of interesting results Notably it shows that an equation of state for nematics can be derived without any intricate thermodynamic arguments and molecular statistical assumptions and that this equation of state reproduces the C and YV results for small length to-breadth ratios as to be expected

The procedure is as follows It is well known that, due to the linear dimensions of the molecules, their centers of mass are excluded from a certain volume The quantity associated with this excluded volume is the packing fraction η For a system of hard spheres we have $\eta = \rho \frac{1}{8} \cdot \frac{4}{3} \pi \sigma^3$, where ρ is the density of the system, σ denotes the diameter of a sphere and $\frac{4}{3} \pi \sigma^3$ is the volume from which the center of mass of a molecule is excluded during a collision between two molecules A straightforward generalization of the equation of state for hard spheres to any type of rigid molecule is therefore to replace 8η by the volume from which the center of mass of such a molecule is excluded, when two of these molecules collide, averaged over the molecular orientational distribution function times the density of the system Besides the mixing entropy due to the orientational freedom of the molecules should be taken into account This idea was applied to the Carnahan and Starling [5] (CS) equation of state, that gives the best fit to the Monte Carlo simulation studies of a hard sphere system

In this letter we restrict ourselves to the nematic–isotropic (N–I) transition due to hard core repulsions In order to compare our results with those of C, YV and Onsager [6] we consider the molecules to be spherocylinders with overall length $L + D$ and diameter D According to Onsager the volume from which the center of mass of a spherocylinder with an orientation denoted by the unit vector a_1 is excluded, when it collides with a second spherocylinder with orientation a_2, is given by

$$v_{excl}(a_1, a_2) = 8v_0 + 12\gamma v_0 |\sin(a_1, a_2)| , \tag{1}$$

where v_0 denotes the volume of a spherocylinder and $\gamma = (L/D)^2 [\pi(1 + \frac{3}{2} L/D)]^{-1}$ Next we replace the packing fraction η in CS by $\frac{1}{8}\rho\langle v_{excl}(a_1, a_2)\rangle$ with $\rho = N/V$, where N is the number of spherocylinders and V the volume of the system The average is taken over the two-particle orientational distribution function In the Mean Field Approximation, which is used throughout this paper, we have

$$\langle v_{excl}(a_1, a_2)\rangle = \iint da_1\, da_2\, f(a_1) f(a_2) v_{excl}(a_1, a_2) \tag{2}$$

$f(a_1)$ denotes the one-particle orientational distribution function and the unit vector a_i specifies the direction of the long axis of molecule i Using the empirical CS expression we obtain the following configurational Helmholtz free energy per molecule

$$\beta f = \ln \rho + 2[1 - \tfrac{1}{8}\rho\langle v_{excl}(a_1, a_2)\rangle]^{-1} + [(1 - \tfrac{1}{8}\rho\langle v_{excl}(a_1, a_2)\rangle)^2]^{-1} - 4 + \int da\, f(a) \ln 4\pi f(a) , \tag{3}$$

where $\int da\, f(a) \ln 4\pi f(a)$ is the orientational (mixing) entropy and $\beta = 1/k_B T$ with T denoting the temperature and k_B Boltzmann's constant The distribution function $f(a)$ is obtained by the usual procedure of minimizing the free energy with respect to $f(a)$. It is clear that all relevant thermodynamic properties and the equation of state follow directly from the expression (3).

In order to compare with the existing equations of state we approximate $\frac{1}{8}\rho\langle v_{excl}(a_1, a_2)\rangle$ by $\eta + \frac{3}{2}\eta\gamma\,[\frac{1}{4}\pi - \frac{5}{32}\pi\langle P_2(a_1 \cdot a_2)\rangle]$, where $\eta = \rho v_0$ is the packing fraction of the spherocylinders and P_2 denotes the second Legendre polynomial, and we expand the configurational Helmholtz free energy per molecule in a series of γ keeping only the linear terms of γ For completeness sake we also give the corresponding free energies per molecule of C and YV Thus we have to compare

$$\text{(CS)}\quad \beta f = \ln \rho + \frac{(3 - 2\eta)}{(1 - \eta)^2} - 3\gamma\eta \frac{(\eta - 2)}{(1 - \eta)^3} [\tfrac{1}{4}\pi - \tfrac{5}{32}\pi\langle P_2(a_1 \cdot a_2)\rangle] - 4 + \int da\, f(a) \ln 4\pi f(a) , \tag{4}$$

$$\text{(C)}\quad \beta f = \ln \rho - \ln(1 - \eta) + \frac{3\eta}{1 - \eta} - 1 + \frac{(4 + q - \frac{1}{2}q^2)\eta^2}{3(1 - \eta)^2}$$

$$+ 6\gamma\eta \frac{1 - \frac{1}{3}(1 - q)\eta}{(1 - \eta)^2} [\tfrac{1}{4}\pi - \tfrac{5}{32}\pi\langle P_2(a_1 \cdot a_2)\rangle] + \int da\, f(a) \ln 4\pi f(a) , \quad q = 2(3L/D + 2)^{-1} , \tag{5}$$

$$\text{(YV)}\quad \beta f = \ln \rho - \ln(1 - \eta) + \frac{3}{2(1 - \eta)^2} - \frac{5}{2} + \tfrac{3}{8}\pi\gamma \frac{\eta}{1 - \eta}\left[1 + \frac{3}{(1 - \eta)^2}\right]$$

$$- \tfrac{15}{32}\pi\gamma\eta \frac{2 + \eta}{(1 - \eta)^2} \langle P_2(a_1 \cdot a_2)\rangle + \int da\, f(a) \ln 4\pi f(a) \tag{6}$$

It is of great numerical advantage to replace the order parameter S by an analytical expression in terms of η and γ Therefore we replaced the constraint $a_i^2 = 1$ by the weaker constraint $\langle a_i^2\rangle = 1$ [7] Then we find

$$S = \tfrac{1}{4} + \tfrac{3}{4}[1 - 4/B(\eta, \gamma)]^{1/2} , \tag{7}$$

with

$$B_{CS} = \frac{45\pi\gamma\eta(2 - \eta)}{32(1 - \eta)^3} , \quad B_C = \frac{45\pi\gamma\eta[1 - \frac{1}{3}(1 - q)\eta]}{16(1 - \eta)^2} , \quad B_{YV} = \frac{45\pi\gamma\eta(2 + \eta)}{32(1 - \eta)^2}$$

Thus simplification can be justified without due consideration, because we are mainly interested in comparing the

Table 1
Comparison between values of S, η_n and η_n/η_l at the N–I transition for several values of γ as obtained by using the two mentioned constraints for a^2 applied to Cotter's expression

γ	$\frac{L+D}{D}$	$a^2 = 1$			$\langle a^2 \rangle = 1$		
		S	η_n	η_n/η_l	S	η_n	η_n/η_l
0.01	1 20	0.43	0 896	1 0001	0 34	0 867	1.0000
0 10	1 84	0 46	0 717	1 0026	0 35	0.648	1.0018
0 20	2 39	0 48	0 629	1.0061	0 35	0.545	1.0040
0 30	2.91	0 49	0.568	1.0098	0 36	0.477	1.0062
0 40	3 41	0.50	0.522	1.0133	0 36	0.427	1.0081
1 00	6 30	0.53	0 363	1.0307	0 37.	0.270	1.0167
5.00	25.21	0.56	0 129	1.0725	0 39	0.081	1.0324

eqs (4), (5) and (6). In order to know the quantitative influence of the replacement on the values of the order parameter and the packing fractions of the nematic state (η_n) and the isotropic state (η_l) at the N–I transition, we also calculated them by solving the self-consistency relation for S using the result of the scaled-particle theory, i.e. eq (5). The values of both procedures are given in table 1

The values of η_n, η_l and S at the N–I transition at a constant pressure p are obtained by solving the equations $p_n = p_l$ and $g_n = g_l$, where g denotes the Gibbs free energy per molecule The results are plotted as a function of γ in figs 1 and 2 Experimentally relevant length-to-breadth ratios for thermotropic nematics lay between roughly 2 ($\gamma = 0$ 13) and 5 ($\gamma = 0$ 73).

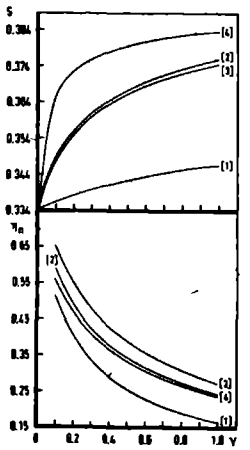

Fig. 1 The values of S and η_n at the N–I transition as a function of γ as obtained from CS not expanded (1), YV (2), C (3) and CS expanded (4).

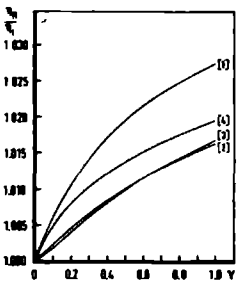

Fig. 2. The value of η_n/η_l at the N–I transition as a function of γ For the meaning of the different lines see the text of fig. 1.

Clearly, expanding the CS expression in γ and keeping only the terms linear in γ gives already results different from those of the original expression for small values of γ. This is not surprising because e.g. a term like $[1 - \frac{1}{8}\rho \times \langle v_{\mathrm{excl}}(a_1, a_2)\rangle]^{-1}$ is approximated by

$$\frac{1}{1-\eta}\left[1 + \frac{3\gamma\eta}{2(1-\eta)}\left(\tfrac{1}{4}\pi - \tfrac{5}{32}\pi S^2\right)\right],$$

where the second term in the square brackets is already of the order 0.2–0.3 for $\gamma \approx 0.3$. In this context it should be noted that Onsager's expression for the configurational Helmholtz free energy follows from the CS expression (3) by an expansion in terms of ρ and keeping only the terms linear in ρ, i.e.

$$\tfrac{1}{2}\rho\langle v_{\mathrm{excl}}(a_1, a_2)\rangle = \eta\left[4 + \tfrac{3}{2}\pi\gamma\left(1 - \tfrac{5}{8}S^2\right)\right].$$

This means that the Onsager theory does not produce reliable quantitative results in the limit of large spherocylinders. For $\gamma \geq 10^3$ Onsager gives at the N–I transition $\gamma\eta_n = 469 \times 10^{-3}$, $\eta_n/\eta_i = 1.0414$ and $S = 0.392$ ($\frac{1}{2}\rho\langle v_{\mathrm{excl}}(a_1, a_2)\rangle = 2$), while the CS expression gives $\gamma\eta_n = 226 \times 10^{-3}$, $\eta_n/\eta_i = 1.0473$ and $S = 0.357$. We remark here that the expressions (4), (5) and (6) yield the same results as Onsager's expression for $\gamma \geq 10^3$.

The underlying not expanded version of the CS expression gives rise to a molecular orientational distribution function of the form. $f(\theta) = \exp[B(\eta, \gamma, S)SP_2(\cos\theta)]$ in contrast to existing theories where $B(\eta, \gamma, S) = B(\eta, \gamma)$, i.e. does not depend on S. Therefore lower values of the order parameter are obtained at the N–I transition. Because the expectation values of the higher order virial terms were roughly decoupled in products of the expectation value of the second virial coefficient, it might be expected that the generalized CS expression overestimates the excluded volume effect of hard spherocylinders with the relevant dimensions.

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CHAPTER III

THE EQUATION OF STATE FOR NEMATICS REVISITED

I. Introduction

The nematic phase is the least ordered liquid crystalline phase and has several properties in common with isotropic fluids. The main difference with the isotropic fluid phase is the characteristic long range orientational ordering of the long axes of the oblong constituent molecules. Clearly a physically significant molecular statistical description of a nematic should include these experimental facts. An important barrier to such a description is the difficulty in dealing with the intermolecular hard core repulsion. At present a satisfactory molecular statistical description of the nematic phase is not available.

It is wellknown that the molecular hard core of simple fluids like Argon can be satisfactorily described by means of a hard sphere. For such a hard sphere system satisfying equations of state exist. They are based upon the Percus-Yevick[1] and the scaled particle theory[2]. In order to describe the nematic phase and the nematic-isotropic (N-I) transition involved, it merits consideration to derive an equation of state for nematics by an appropriate generalization of the equation of state for hard spheres. In the next section such a generalization procedure is proposed and the relevant thermodynamic quantities are given. In Sec. III the predictions of the model are compared with experimental data for *p*-azoxyanisole (PAA), *p*-methoxybenzylidene-*p*'-butylaniline (MBBA), *p*-methoxybenzylidene-*p*'-cyanoaniline (MBCA) and a number of homologues of alkyl-cyano-biphenyl (nCB,n=5-9, $C_nH_{2n+1}.\phi.\phi.CN$) and anisylidene-*p*-aminophenylacetate (APAPAn,n=1-9, $CH_3O.\phi.CHN.\phi.OCOC_nH_{2n+1}$). In the case of PAA the model calculations are also compared with those of Cotter[3] and Ypma et al.[4]. Finally, in Sec. IV, an evaluation of this phenomenological approach is given and conclusions are drawn.

II. Model

The general expression for the hard core equation of state for spheres is given by

$$pV/NkT = K(\eta) \tag{2.1}$$

where p denotes the pressure, V is the volume of the system, N is the number of spheres, k is Boltzmann's constant, T is the temperature, η is the packing fraction and $K(\eta)$ is some function of η. It is clear that the packing fraction η is related to the molecular linear dimensions, the intermolecular interactions and the eventual attending correlations between the orientations of the molecules. The relevant quantity associated with the linear dimensions of a molecule is the excluded volume v_{excl}, being defined as that part of space from which the center of mass of a given molecule is excluded during a collision with a second molecule. In the case of hard spheres with diameter σ we have

$$\rho v_{excl} = \rho \frac{4\pi}{3} \sigma^3 \equiv 8\eta \tag{2.2}$$

where $\rho = N/V$ denotes the particle number density.

The equation of state for hard spheres can be generalized in a straightforward manner to any type of rigid molecule through the replacement

$$8\eta \rightarrow \rho \langle v_{excl} \rangle$$

where the brackets denote an average over the two-particle orientational distribution function. Our phenomenological derivation of the hard core equation of state for nematics is based upon this recipe. The natural candidate for the function $K(\eta)$ is the expression given by Carnahan and Starling[5]

$$K(\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{2.3}$$

because of its excellent agreement with molecular-dynamics studies for hard spheres. The expression for the hard core part of the free energy is simply obtained by integrating the thermodynamic relation $p=-(\frac{\partial F}{\partial V})_{T,N}$ and adding the mixing entropy due to the orientational freedom of the molecules.

In selecting a physically acceptable hard core for the constituent molecules of a nematic, the following experimental facts should play a part:

a) A long axis can be uniquely adjusted to the molecules of a nematic. The molecules rotate rapidly around these axes. Thus the molecules are effectively cylindrical symmetric with respect to their long axes in a first approximation.

b) Nematics do not show ferroelectric effects on a macroscopic scale, although the constituent molecules may be polar, e.g. PAA. In a first approximation therefore "head-tail" effects can be neglected.

In accordance with these facts we choose, like Onsager[6] and many other authors, a spherocylindrical molecular hard core in order to keep the mathematics as simple as possible.

A crude way of taking into account the molecular structure of a nematogen is to assume an attractive intermolecular interaction which depends upon the mutual orientation. Such a type of interaction has to be included in order to account for, at least partially, the differences between nematics consisting of molecules with the same length but a different molecular structure. Likewise an isotropic intermolecular attraction should be assumed in order to obtain a meaningful description of the isotropic phase.

In the following calculations a simple attractive intermolecular interaction is used. Analogous to Cotter and Ypma et al. we take the following attractive interaction u_{ij} between molecules i and j

$$u_{ij} = -\frac{1}{V}\,(J_0 + J_2 P_2(\vec{a}_i \cdot \vec{a}_j)) \tag{2.4}$$

where the unit vectors $\vec{a}_i$ and $\vec{a}_j$ specify the direction of the long axis of molecule i and j respectively and P_2 denotes the second Legendre polynomial given by $P_2(x) = \frac{1}{2}(3x^2-1)$. The interaction constants J_0 and J_2 are divided by the volume V of the system in order to get an extensive expression for the energy. The interaction $\frac{-J_0}{V}$ is introduced in order to describe the isotropic fluid, whereas the interaction $\frac{-J_2}{V} P_2(\vec{a}_i.\vec{a}_j)$ helps along the appearance of the anisotropic fluid. The interaction strength J_2 might be correlated amongst others with the anisotropic polarizability [7] and the isotropic intermolecular interaction and the shape of the molecules[8]. Treating both repulsive and attractive forces in the mean field approximation the following expression for the Helmholtz free energy per molecule f is obtained:

$$\beta f = 3\ln\lambda + \beta f_c - \frac{\beta J_0}{2v_o}\eta - \frac{\beta J_2}{2v_o}\eta \int d\vec{a}_1 d\vec{a}_2 f(\vec{a}_1) f(\vec{a}_2) P_2(\vec{a}_1.\vec{a}_2) \qquad (2.5)$$

where $\lambda = h[2\pi mkT]^{-\frac{1}{2}}$ is the so called de Broglie wavelength with h denoting Planck's constant and m the molecular mass. The packing fraction η equals $Nv_o/V = \rho v_o$ with v_o denoting the volume of a molecule and $\beta = 1/kT$. The molecular hard core Helmholtz free energy per molecule f_c reads in the mean field approximation

$$\beta f_c = \ln\rho + \frac{3-2\tau}{(1-\tau)^2} - 4 + \int d\vec{a} f(\vec{a}) \ln 4\pi f(\vec{a}) \qquad (2.6)$$

where

$$\tau \equiv \frac{\rho}{8} \langle v_{excl}(\vec{a}_1,\vec{a}_2)\rangle = \frac{\rho}{8} \iint d\vec{a}_1 d\vec{a}_2 f(\vec{a}_1) f(\vec{a}_2) v_{excl}(\vec{a}_1,\vec{a}_2) \qquad (2.7)$$

and $f(\vec{a})$ denotes the one-particle orientational distribution function, which is determined by minimization of the free energy with respect to this function. The term $\int d\vec{a} f(\vec{a}) \ln 4\pi f(\vec{a})$ is called the orientational mixing entropy. The long range order parameter S is determined by

$$S = \int P_2(\vec{a}.\vec{n}) f(\vec{a}) d\vec{a} \tag{2.8}$$

where the unit vector $\vec{n}$ specifies the direction of the average orientation of the molecules (director). The excluded volume of two spherocylinders with diameter D, overall length L + D and orientations $\vec{a}_1$ and $\vec{a}_2$ respectively is given by

$$v_{excl}(\vec{a}_1,\vec{a}_2) = 8v_o + 12\gamma v_o |\sin(\vec{a}_1,\vec{a}_2)| \tag{2.9}$$

where

$$\gamma = \frac{2(x-1)^2}{\pi(3x-1)} \tag{2.10}$$

with

$$x = (L + D)/D \tag{2.11}$$

In order to keep the mathematics simple as well as to be able to compare our results with Cotter's PAA-results, we approximate the excluded volume by putting

$$\langle |\sin(\vec{a}_1,\vec{a}_2)| \rangle = \frac{\pi}{4} - \frac{5\pi}{32} \langle P_2(\cos(\vec{a}_1,\vec{a}_2)) \rangle = \frac{\pi}{4} - \frac{5\pi}{32} S^2 \tag{2.12}$$

As is known[3], this approximation influences the quantitative results for S and the other thermodynamic quantities. However, in view of the approximations used to arrive at the equation (2.5) for the free energy, only a qualitative understanding of nematics can be hoped for by means of the present model. From this point of view the approximation (2.12) is allowed. Now the one-particle orientational distribution function $f(\vec{a})$, which is determined by minimizing the free energy with respect to this function, reads

$$f(\vec{a}) = \frac{1}{4\pi Z} \exp\left[\left(\frac{15\pi\eta\gamma[2-\tau]}{16(1-\tau)^3} + \frac{\beta J_2 \eta}{v_o}\right) S P_2(\vec{a}.\vec{n})\right] \tag{2.13}$$

where

$$\tau = \eta + \frac{3}{2}\gamma\eta\left(\frac{\pi}{4} - \frac{5\pi}{32} S^2\right) \tag{2.14}$$

and Z is a normalization constant such that $\int d\vec{a} f(\vec{a}) = 1$. Clearly the orientational distribution function (2.13) depends on S in a more intricate way than the corresponding expressions in the calculations of Cotter and Ypma. For the sake of completeness we give here the expressions for the pressure p,

$$p = -\tfrac{1}{2}J_0\rho^2 - \tfrac{1}{2}J_2 S^2\rho^2 + \rho kT\frac{(1+\tau+\tau^2-\tau^3)}{(1-\tau)^3} \tag{2.15}$$

and the Gibbs free energy per molecule $g = \frac{G}{N}$,

$$\beta g = 3\ln\lambda + \ln\rho - 4 - \beta J_0\rho + \frac{15\pi}{16}\eta\gamma\frac{(2-\tau)}{(1-\tau)^3} S^2 + \frac{(4-4\tau+3\tau^2-\tau^3)}{(1-\tau)^3} - \ln Z \tag{2.16}$$

III. Results

First we apply our model to PAA. Analogous to Ypma we treat J_0, J_2 and x as parameters. In order to investigate the usefulness of the model we determine these parameters in two different ways. The parameters are chosen such that the observed values of the following two sets of quantities are reproduced

A) T_{NI}, η_{nNI} and $\Delta\eta_{NI}/\eta_{iNI}$

B) T_{NI}, η_{nNI} and $\Gamma(T_{NI})$,

while we further keep the pressure p fixed at one atmosphere and use a molecular volume $v_o = 230 Å^3$ as estimated by Vieillard-Baron[9]. T_{NI} denotes the nematic-isotropic transition temperature, η_{nNI} is the nematic packing fraction at T_{NI} and $\Delta\eta_{NI}/\eta_{iNI}$ denotes the corresponding relative volume change. The quantity $\Gamma(T)$ is defined as

$$\Gamma(T) = \frac{V(\partial S/\partial V)_T}{T(\partial S/\partial T)_V} = \frac{\eta}{T}\left(\frac{\partial T}{\partial \eta}\right)_S \tag{3.1}$$

and measures the relative sensitivity of the order parameter S to volume changes (at a constant temperature) and temperature changes (at a constant volume). In the case of a distance-independent attractive potential as given in (2.4) it follows that

$$\Gamma(T) = 1 + \frac{\gamma T k v_o}{J_2} \Lambda(\eta_n, x, S) \tag{3.2}$$

The function Λ depends upon S in the present model in contrast to the models of Cotter[3] and Ypma et al.[4]. In the present model the function Λ is given by

$$\Lambda(\eta, x, S) = \frac{15\pi(2+2\tau-\tau^2)}{16(1-\tau)^4} \tag{3.3}$$

where τ is given by (2.14). Clearly then spherical-shaped molecules always give $\Gamma(T) = 1$ using a distance-independent attractive potential. More important to note is $\Gamma(T) = \infty$ for all x if $J_2 = 0$. This means that the parameter $\Gamma(T)$, being equal to 2.6 for MBBA[10], 6 for 5CB[10] and nearly 4 for PAA[11], indicates clearly the importance of the orientation-dependent part of the interaction (2.4) in order to describe the nematic phase. Treating x as a parameter in the calculations is plausible because

a) the real molecules do not have a rigid spherocylindrical form;

b) the excluded volume effect is overestimated due to the fact that the expectation

value of the higher order virial terms is approximated by products of the expectation value of the second virial coefficient.

In Table I the values of several thermodynamic quantities at the N-I transition are given at a pressure of one atmosphere using the parameters J_0, J_2 and x determined according to the procedures A and B. These values are obtained by solving the equations $p_N=p_I=1$ atm , $g_N=g_I$, and the equation (2.8) for the order parameter. Likewise the heat of vaporization ΔH_{IG} and the boiling temperature T_b of PAA are calculated by solving $p_I=p_G=1$ atm and $g_I=g_G$ where p_G denotes

TABLE I: Comparison between the experimental data concerning the N-I and I-G transition in PAA and the results obtained from the Ypma (Y), Cotter (C) and present model. A and B refer to two different fit procedures explained in the text.

$(J_0/kv_o)_A$=42540°K; $(J_2/kv_o)_A$=2918°K; x_A = 1.099

$(J_0/kv_o)_B$=49731°K; $(J_2/kv_o)_B$=1989°K; x_B = 1.380

$(J_0/kv_o)_Y$=39000°K; $(J_2/kv_o)_Y$=1850°K; x_Y = 1.464

$(J_0/kv_o)_C$=25000°K; $(J_2/kv_o)_C$=2000°K; x_C = 3.000

	Present model				
Quantity	A	B	Ypma et al.	Cotter	PAA
T_{NI}	409.0°K	409.0°K	409°K	410.4°K	409°K[7]
S_{NI}	0.437	0.452	0.473	0.542	0.40[12]
η_{nNI}	0.620	0.6205	0.596	0.445	0.62[7,9]
$\Delta\eta_{NI}/\eta_{iNI}$	0.0035	0.0069	0.0102	0.040	0.0035[7]
$\Delta\Sigma/Nk$	0.536	0.567	0.590	0.887	0.17[13]
$\Gamma(T_{NI})$	1.16	4.00	3.96	3.90	4.0[11]
$(dT_{NI}/dp)_{p=1atm}$	17.6°K/kbar	32.8°K/kbar	48.6°K/kbar	175°K/kbar	48°K/kbar[14]
T_b	1105.1°K	1240.4°K	—	—	—
ΔH_{IG}	84242J/mole	95978J/mole	—	—	73750J/mole[15]

the vapourpressure and g_G is the Gibbs free energy per molecule in the gaseous phase. The pressure dependence of the transition temperature, dT_{NI}/dp, is determined by means of Clausius-Clapeyron's law. The results of Cotter and Ypma et al. together with the experimental data for PAA are also presented in Table I.

A few remarks should be made about the values of some quantities given in Table I. The value of x_Y is obtained by using equation (2.40) of reference 4. The results of Cotter, shown in column 5 of Table I, support our arguments for treating x as a parameter. Using only J_0 and J_2 as parameters and assuming the

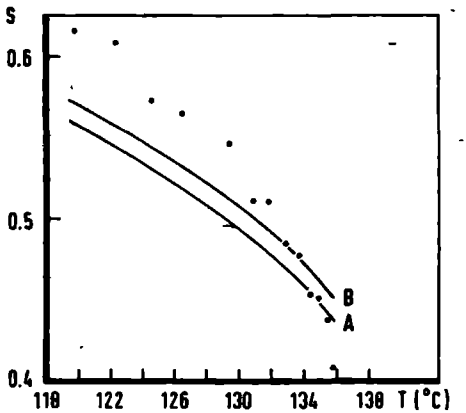

FIG. 1: The order parameter S of PAA as a function of temperature at a constant pressure of one atmosphere. The curves A and B concern the calculation procedures A and B described in the text. The dots denote the experimental data of Lippmann[16].

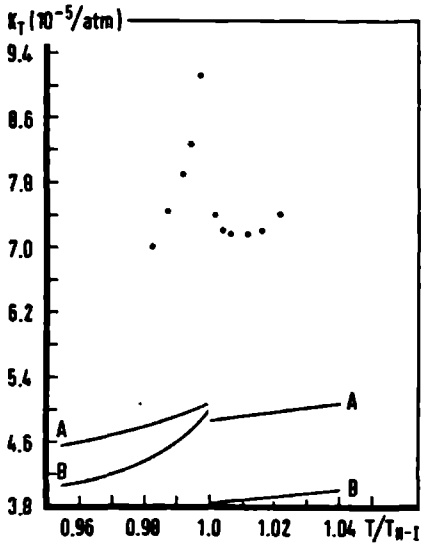

FIG. 2: The isothermal compressibility K_T of PAA as a function of the reduced temperature T/T_{NI}. The curves A and B concern the calculation procedures A and B described in the text. The experimental data of Kapustin and Bykova[17] *are denoted by dots.*

more realistic value x = 3 for the length-to-breadth ratio of PAA, less favourable results are obtained. Obviously our predictions for the boiling temperature are doubtful because the real molecules might be already disintegrated at these temperatures. Experimental data on the boiling temperature are not known to us.

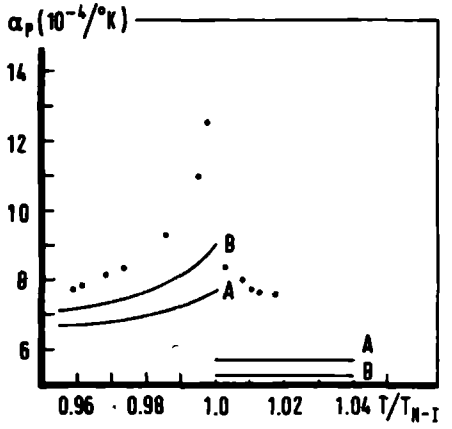

FIG. 3: *The isobaric thermal expansitivity α_p of PAA as a function of the reduced temperature T/T_{NI}. The curves A and B concern the calculation procedures A and B described in the text. The experimental data are those of Maier and Saupe[7].*

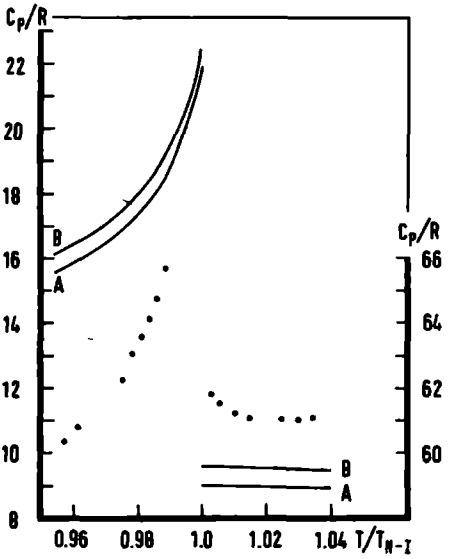

FIG. 4: *The specific heat C_p of PAA as a function of the reduced temperature T/T_{NI}. R denotes the molar gasconstant. The curves A and B concern the calculation procedures A and B described in the text. The experimental values of C_p are taken from Arnold[13]. It should be noted that the right-hand-side-scale only applies to the experimental data whereas the left-hand-side-scale concerns the curves A and B.*

It follows from Table I that the predictions of the model are rather sensitive to the quantities that are selected to determine the parameters J_2, J_0 and x. This conclusion is further supported by considering the temperature dependence of the order parameter S, and the reduced temperature dependence of the isothermal compressibility K_T, the isobaric thermal expansitivity α_p and the specific heat C_p using the values of J_0, J_2 and x as obtained from the procedures A and B. The results are shown in Figs. 1-4 together with the available experimental data for PAA. It is clear that the present model gives, just like the Cotter and Ypma model, only an approximate description.

The above mentioned conclusion is also sustained by a calculation of the values of several thermodynamic quantities of MBBA and 5CB at the N-I transition at a pressure of one atmosphere using the parameters J_0, J_2 and x determined according to the procedures A and B. The results are presented in Table II. Here it is seen that a spherical hard core gives rise to the best fit for MBBA and 5CB using the procedure A. This rather unsatisfactory result is not surprising because of the value of S_{NI} and the smallness of the relative density change at the transition in these materials. The present model, just like the Cotter and Ypma models, does not give rise to such a behaviour, due to the fact that S_{NI} is always larger than 0.429 and increases with x. A small density change in these models can only be obtained at the cost of a considerable worsening of the values of the remaining quantities at the transition, e.g. the order parameter.

Next we compare two nematogens with a rigid molecular structure, namely APAPA and MBCA. Because of lack of sufficient experimental data the parameters J_0, J_2 and x can only be determined by means of the observed values of η_{nNI}, T_{NI}, $\Delta\eta_{NI}/\eta_{iNI}$, the calculated molecular volumes v_o and the given pressure of one atmosphere (procedure A). The results of our calculations and the available experimental data are given in the Tables III and IV. Obviously the model gives only a partly correct description of the mutual differences among both nematics as follows from the predicted behaviour of the packing frac-

TABLE II: Comparison between the experimental data concerning the N-I transition in MBBA and 5CB, and the model results. A and B refer to two different fit procedures explained in the text.

	MBBA			5CB		
	Model		Experiment	Model		Experiment
Parameter	A	B		A	B	
J_0/kv_o	46735°K	45813°K		36776°K	41656°K	
J_2/kv_o	2166°K	1773°K		2186°K	1233°K	
κ	1.00	1.24		1.00	1.42	
Quantity						
T_{NI}	318.2 °K	318.2 °K	318.2[18]	308.2 °K	308.2 °K	308.2°K[22]
S_{NI}	0.432	0.441	0.31[19]	0.434	0.454	0.377[23]
η_{nNI}	0.668	0.654	0.655[19]	0.641	0.630	0.63[22]
$\Delta\eta_{NI}/\eta_{iNI}$	0.0016	0.0037	0.0013[19]	0.0024	0.0073	0.0010[22]
$\Delta\Sigma/Nk$	0.504	0.527	0.12[20]	0.518	0.567	0.20[10]
$\Gamma(T_{NI})$	1.00	2.60	2.6[10]	1.00	6.0	6[10]
$(dT_{NI}/dp)_{p=1atm}$	9.8°K/kbar	21.9°K/kbar	∿33°K/kbar[21]	13.3°K/kbar	38.1°K/kbar	37.2°K/kbar[10]

TABLE III: Comparison between the experimental data concerning the N-I and I-G transition in MBCA, APAPA and 9CB, and the model results.

Parameter	MBCA		APAPA		9CB	
J_0/kv_o	48683°K		45418°K		34066°K	
J_2/kv_o	2420°K		2523°K		2256°K	
x	1.210		1.168		1.130	
Quantity	Model	Experiment	Model	Experiment	Model	Experiment
T_{NI}	391.2°K	391.2°K[19]	384.2°K	384.2°K[19]	322.7°K	322.7°K[22]
S_{NI}	0.4401	0.43[19]	0.4384	0.39[19]	0.4380	0.470[23]
η_{nNI}	0.638	0.638[19]	0.634	0.634[19]	0.6207	0.6207[22]
$\Delta\eta_{NI}/\eta_{iNI}$	0.0038	0.0038[19]	0.0035	0.0035[19]	0.0037	0.0037[22]
$\Delta\Sigma/Nk$	0.533	0.186[19]	0.531	0.171[19]	0.537	—
$\Gamma(T_{NI})$	1.92	—	1.54	—	1.27	—
$(dT_{NI}/dp)_{p=1atm}$	18.9°K/kbar	—	19.5°K/kbar	—	26.1°K/kbar	—
T_b	1239.5°K	—	1181.2°K	—	940.7°K	—
ΔH_{IG}	96032J/mole	—	89188J/mole	—	65094J/mole	—

tion η and the order parameter S as a function of the reduced temperature. Further it seems worthwile to comment on the values of x in Table III. According to this table the "renormalized" length-to-breadth ratio of APAPA is smaller than that of MBCA. Calculations of Leenhouts[19], however, indicate the opposite ($x_{MBCA} = 2.92$, $x_{APAPA} = 3.25$). It seems therefore questionable to interpret the parameter x in terms of a renormalized length-to-breadth ratio.

Finally we examine whether the present model is able to describe the trends observed in two homologous series, namely the homologous series APAPAn, n=1-9, measured by Leenhouts et al.[18,19] and the homologous series nCB, n=5-9, measured by Dunmur and Miller[22] and Sherrel and Crellin[23]. Taking into account the odd-even effect one may roughly state that S_{NI}, $\Delta\eta_{NI}/\eta_{iNI}$, η_{nNI} and T_{NI}

TABLE IVa: The order parameter S and the packing fraction η of APAPA as a function of the reduced temperature T/T_{NI} at a constant pressure of one atmosphere. The experimental data, denoted by the subscript exp, are taken from Leenhouts[19].

		APAPA			
	T/T_{NI}	S_{th}	S_{exp}	η_{th}	η_{exp}
Nematic phase	0.97	0.538	0.55	0.639	0.642
	0.98	0.512	0.52	0.638	0.640
	0.99	0.481	0.47	0.636	0.637
	1.00	0.438	0.39	0.634	0.634
Isotropic phase	1.00	0	0	0.632	0.632
	1.01	0	0	0.630	0.629

TABLE IVb: The order parameter S and the paking fraction η of MBCA as a function of the reduced temperature T/T_{NI} at a constant pressure of one atmosphere. The experimental data, denoted by the subscript exp, are obtained from reference 19.

		MBCA			
	T/T_{NI}	S_{th}	S_{exp}	η_{th}	η_{exp}
Nematic phase	0.97	0.539	0.65	0.643	0.646
	0.98	0.513	0.62	0.642	0.644
	0.99	0.482	0.57	0.640	0.641
	1.00	0.440	0.43	0.638	0.638
Isotropic phase	1.00	0	0	0.636	0.636
	1.01	0	0	0.634	0.634

decrease with increasing n within the homologous series of APAPA, while the homologues of CB show an increase of S_{NI}, T_{NI}, $\Delta\eta_{NI}/\eta_{iNI}$ and a decrease of η_{nNI} with increasing n. Obviously these more or less opposite tendencies stress the relevance of such an analysis.

Unfortunately the number of available experimental data is also rather limited here except for 5CB (see Table II). Hence we are forced to apply the same calculation procedure as used for MBCA and APAPA. The results of these calculations and the experimental data are given in the Tables V and VI. The required molecular volumes have been taken from Leenhouts[19] and Dunmur and Miller[22]. The values of the entropy change at the transition $\Delta\Sigma$ are determined via the relation $\Delta H_{NI} = T_{NI}\Delta\Sigma$, where ΔH_{NI} denotes the latent heat. Table V, which concerns the homologues of APAPA, shows a number of physical shortcomings of the present model. A quite serious shortcoming is the result that a spherical hard core gives rise to the best fit, except in the case of APAPA (see Table III). For reasons of comparison, however, a spherical hard core fit for APAPA is also incorporated in Table V. The observed and the predicted trends for η_{nNI} and $\Delta\Sigma/Nk$ do not agree. Besides S_{NI} is nearly a constant for all homologues of APAPA. As for the homologues nCB, n = 5–9, the predicted trends agree with the available experimental ones but the shortcoming of a best fit with a sperical hard core remains. The fact that a spherical hard core give rise to the best fit for both series, is not surprising, because of the low values of the order parameters and the relative density changes at the transition. In this context it should be remarked that Dunmur and Miller[22] did a similar type of theoretical analysis for nCB, n = 5–9, using Cotter's model[3]. Their results, however, are not reliable because they obtained values for S_{NI}, which are all less than 0.429.

Lower values for the order parameter S_{NI} and the entropy change $\Delta\Sigma/Nk$ at the transition can be obtained by means of approximation methods, that go beyond the molecular field approximation, e.g. the two-site cluster approxima-

TABLE V: Comparison between the calculated values of a number of quantities at the N-I transition of the homologues APAPAn (n = 1-9) and the experimental results of Leenhouts et al.[18,19]. The best fit is obtained by using hard spheres, i.e. x = 1. The calculated molecular volumes v_o are also taken from Leenhouts.

n	v_o(Å^3)	T_{NI}(°C)	J_0/kv_o(°K)	J_2/kv_o(°K)	S_{NI}^{th}	S_{NI}^{exp}	η_{nNI}^{th}	η_{nNI}^{exp}	$\Delta\eta_{NI}/\eta_{iNI}^{th}$	$\Delta\eta_{NI}/\eta_{iNI}^{exp}$	$\Delta\Sigma/Nk^{th}$	$\Delta\Sigma/Nk^{exp}$
1	258	111.0	40188	2805	0.4354	0.39	0.623	0.634	0.0030	0.0035	0.530	0.17
3	292	112.8	41365	2803	0.4351	0.35	0.626	0.624	0.0029	0.0028	0.528	0.20
5	326	103.2	42619	2700	0.4345	0.37	0.634	0.623	0.0026	0.0022	0.523	0.21
7	360	98.8	40691	2689	0.4349	0.35	0.629	0.622	0.0028	0.0025	0.526	0.21
9	395	96.5	41528	2656	0.4346	0.32	0.633	0.621	0.0027	0.0022	0.523	0.25
2	275	110.6	44012	2745	0.4344	0.33	0.636	0.629	0.0025	0.0023	0.522	0.15
4	309	100.0	43095	2665	0.4343	0.33	0.637	0.628	0.0025	0.0022	0.521	0.15
6	343	97.1	43733	2632	0.4341	0.34	0.640	0.625	0.0024	0.0019	0.519	0.19
8	377	93.7	41104	2638	0.4346	0.30	0.633	0.623	0.0027	0.0023	0.524	0.22

TABLE VI: Comparison between the calculated values of a number of quantities at the N-I transition of the homologues nCB (n = 5-9) and the experimental data of Sherrell et al.[23] (S_{NI}), of Karat et al.[24] ($\Delta\Sigma/Nk$), and those of Dunmur et al.[22]. The calculated molecular volumes v_o are taken from Dunmur et al. The best fit is obtained by using hard spheres, i.e. x = 1.

n	v_o (Å^3)	T_{NI} (°C)	J_0/kv_o (°K)	J_2/kv_o (°K)	S_{NI}^{th}	S_{NI}^{exp}	η_{nNI}^{th}	η_{nNI}^{exp}	$\eta_{nNI}/\eta_{iNI}^{th}$	$\eta_{nNI}/\eta_{iNI}^{exp}$	$\Delta\Sigma/Nk^{th}$	$\Delta\Sigma/Nk^{exp}$
5	258	35.0	36776	2186	0.4340	0.377	0.641	0.631	1.0024	1.0020	0.518	0.14
7	291	42.7	35834	2265	0.4345	0.369	0.634	0.623	1.0026	1.0022	0.523	0.22
9	325	49.5	31811	2389	0.4362	0.470	0.615	0.621	1.0034	1.0037	0.536	--
6	275	29.4	42098	2081	0.4328	0.336	0.661	0.631	1.0018	1.0010	0.507	0.10
8	308	40.6	37870	2220	0.4339	0.348	0.643	0.624	1.0023	1.0017	0.517	0.27

tion[4]. A far more simple method, however, to obtain lower values for both quantities is through replacing the unit vector $\vec{a}$ by a Gaussian distribution of vectors $\vec{a}$ having $\langle\vec{a}^2\rangle = 1$, i.e. the standard deviation of this distribution equals one[25,26]. Then the model is able to reproduce the experimental values of T_{NI}, η_{nNI} and η_{iNI} for each nematic in question. Figs. 5a and 5b show the results for S_{NI} and $\Delta\Sigma/Nk$ respectively in the case of the homologues of APAPA. The experimental data with their estimated errors are also shown in these figures. The values of the model parameters J_0, J_2 and x are given in

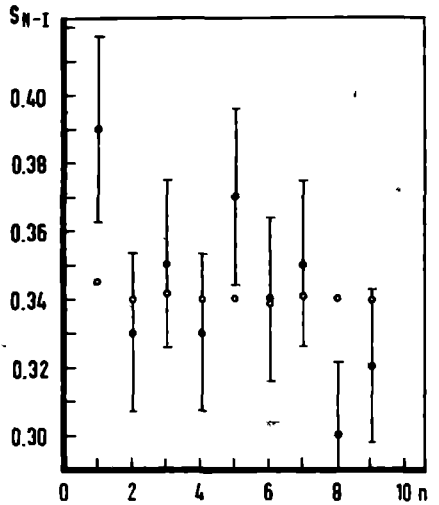

FIG. 5a: The value of the order parameter S_{NI} as a function of the number of carbon atoms of the alkyl chain for the homologues of APAPA. The theoretical values (open circles) are obtained from the present model using $\langle\vec{a}^2\rangle=1$. The values of the model parameters J_0, J_2 and x are given in Table VII. The experimental data are taken from Leenhouts et al.[18].

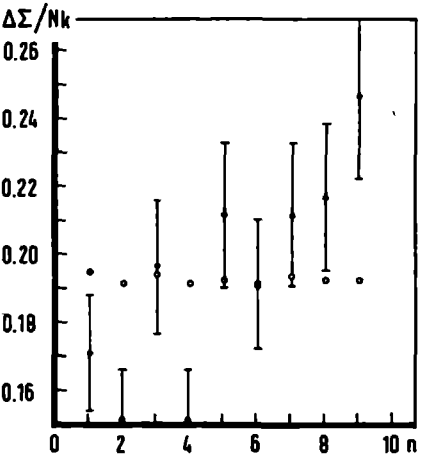

FIG. 5b: The value of the entropy change $\Delta\Sigma/Nk$ at the N-I transition as a function of the number of carbon atoms of the alkyl chain for the homologues of APAPA. The theoretical values (open circles) are obtained from the present model using $\langle\vec{a}^2\rangle=1$. The values of the model parameters J_0, J_2 and x are given in Table VII. The experimental data are taken from Leenhouts[19].

Table VII. Although S_{NI} and $\Delta\Sigma/Nk$ have now the correct magnitude for a number of homologues, the observed trends are still not qualitatively described by the model. Further it should be remarked that the irregular behaviour of the parameter x within the APAPA-series makes its interpretation in terms of an

TABLE VII: The values of the model parameters J_0/kv_o, J_2/kv_o and x used to obtain the theoretical results shown in Fig. 5a and Fig. 5b.

	x	J_0/kv_o (°K)	J_2/kv_o (°K)
APAPA	1.410	54102	396
APAPA 3	1.326	47056	925
APAPA 5	1.253	43395	1181
APAPA 7	1.289	43539	1051
APAPA 9	1.250	41909	1183
APAPA 2	1.276	46934	1084
APAPA 4	1.262	44887	1111
APAPA 6	1.216	42399	1264
APAPA 8	1.266	42632	1109

TABLE VIII: The reduced temperature dependence of the order parameter S in the case of APAPAn, n = 1,3,5,7 and 9, using the model with $\langle \vec{a}^2 \rangle = 1$. The values of J_0/kv_o, J_2/kv_o and x are given in Table VII.

T/T_{NI}	$S_{n=1}$	$S_{n=3}$	$S_{n=5}$	$S_{n=7}$	$S_{n=9}$
0.96	0.446	0.443	0.441	0.442	0.441
0.97	0.426	0.424	0.422	0.423	0.422
0.98	0.405	0.402	0.400	0.401	0.400
0.99	0.379	0.376	0.374	0.375	0.374
1.00	0.346	0.342	0.340	0.341	0.340

effective molecular length-to-breadth ratio highly questionable. A trend for the coupling parameters J_0/kv_o and J_2/kv_o is not observed. Such a trend does not appear for the homologues nCB, n = 5-9, either. Finally the discrepancy should be pointed out between the experimental and calculated dependence of the order parameter S on the reduced temperature for the homologues APAPAn with n = 1,3, 5,7 and 9. The results of the calculations are shown in Table VIII. According to the theory the order parameter of APAPA is always larger than the order parameter of APAPA9 using the reduced temperature scale. Experimentally, however, both curves intersect.

IV. Summary and conclusions

A phenomenological equation of state for nematics is derived via a very simple straight-forward generalization of the Carnahan-Starling equation of state for hard spheres. This type of approach has two advantages over the approaches of Cotter and Ypma:

a) The derivation of the equation of state is quite simple.

b) Problems that are met in the scaled particle approach of Cotter concerning thermodynamic consistency or in the approach of Ypma concerning the interpretation of the eccentricity parameter, are absent.

A comparison between the three approaches shows that the phenomenological equation of state describes PAA at least equally well as the equation of state of Ypma, which gives already a fairly good description of PAA. Further the present model gives a qualitatively correct description of the trends, that are observed so far, within the series of homologues nCB with n = 5-9. The description, however, presents also conceptual difficulties in the sense that a spherical hard core gives rise to the best fit. This entails $\Gamma(T) = 1$, which does not hold experimentally at least not for 5CB. This situation can be partly remedied through replacing $\vec{a}^2 = 1$ by the weaker constraint $\langle\vec{a}^2\rangle = 1$.

It appears that the present model does not give a qualitatively correct description of the mutual differences between rigid molecules like APAPA, MBCA and PAA. Further the model is not able to predict observed trends concerning the values of the order parameter and the change in entropy at the N-I transition as far as the homologues APAPAn (n = 1-9) are concerned. Moreover it seems highly questionable to interpret the parameter x in terms of a "renormalized" length-to-breadth ratio as follows from the values of x for the rigid nematogens APAPA, MBCA and PAA and the irregular behaviour of x in the case of the homologues APAPAn (n = 1-9).

The discrepancies between theory and experiment may be attributed to the following reasons:

a) The real influence of the intermolecular hard core repulsion is very difficult to calculate. In the present model the expectation values of the higher order virial terms are approximated by products of the expectation value of the second virial coefficient. This procedure is clearly too rough and overestimates the excluded volume effect. The overestimation seems to manifest itself in the predicted low values of the length-to-breadth ratio of the molecules. In this context it should be remarked that the approach of Ypma et al. is less transparant as far as the excluded volume effect is concerned because of the introduction of an eccentricity parameter. Interpretation of this parameter in terms of the real length-to-breadth ratio shows that the Ypma approach just like Cotter's approach overestimates the excluded effect as well. In order to improve the hard core equation of state one faces at least a three body problem, an extremely difficult problem in the case of oriented non-spherical molecules.

b) The calculations are performed in the mean field approximation. This means that a number of quantities are overestimated at the transition, e.g. the jump in the order parameter and the change in entropy. Likewise the tem-

perature dependence of quantities like K_T etc. is incorrectly described in the neighbourhood of the N-I transition. It is not to be expected, however, that a more sophisticated approximation would reverse the trends shown by the molecular field calculations.

c) The molecular structure is only very roughly taken into account using a potential like (2.4).

d) A spherocylincrical molecular hard core is not satisfactory from a chemical point of view. The flexibility of the molecules should be taken into account, e.g. the flexibility of the homologues APAPAn. The results that are obtained for the APAPA-series using the constraint $\langle \vec{a}^2 \rangle = 1$, point out that more parameters are needed in order to describe all trends within this series. One of these parameters should probably account for the flexibility of the molecules.

In conclusion, it may be stated that this paper shows clearly the difficulties, that should be coped with, in order to arrive at a really satisfying equation of state for nematics. Notably it stresses the importance of the inclusion of molecular flexibility and of a better treatment of the molecular hard core repulsion and molecular structure in the description of nematics.

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CHAPTER IV

EQUATION OF STATE FOR NEMATICS HAVING A CYLINDRICAL HARD CORE

The great majority of nematics, that are studied, consist of molecules with an oblong structure. In molecular statistical theories this quite complicated structure is replaced, as far as its repulsive interaction is concerned, by a spherocylinder in order to keep the mathematics as simple as possible. Clearly a spherocylinder cannot describe nematics consisting of molecules with a disc-like structure [1], because the overall length-to-breadth ratio x of a spherocylinder ranges from one, a sphere, to infinity. The purpose of this chapter is to give an approximate description of a system consisting of hard cylinders. By conceiving the molecular structure of the constituent molecules of nematics as a hard cylinder both oblong and disc-like molecules can be described by varying the length-to-breadth ratio x from small values (discs) to large values (oblong cylinders). Up to the present the nematic-isotropic (N-I) transition in a system of hard cylinders has been only studied by means of the approximation of Onsager for the free energy [2,3,4]. The Onsager expression, however, is of limited value. It is true that it gives a qualitatively correct description in the limit of small and large values of x, but further it produces unphysical results in the interesting intermediate region $0.05 < x < 20$ [4].

The derivation of the equation of state for a system consisting of hard cylinders is an extremely difficult molecular statistical problem. Nevertheless it is possible to gain a good insight into the thermodynamic behaviour of the system by means of an appropriate generalization of the well tested equation of state for a system of hard spheres. This generalization procedure, which was already applied successfully to a system of hard spherocylinders [5], boils down to the following. The starting point is the equation of state for hard spheres

$$\frac{pV}{NkT} = K(\eta) \qquad (1)$$

with p denoting the pressure, V the volume of the system, N the number of

spheres, k Boltzmann's constant, T the temperature, η the packing fraction and $K(\eta)$ some function of η. For the function $K(\eta)$ we take the expression of Carnahan and Starling [6]

$$K(\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{2}$$

because of its excellent agreement with the molecular dynamics results for hard spheres. The packing franction η enters the equation of state because the molecules have a volume of their own. This volume gives rise to an excluded volume v_{excl}, which is defined as that part of space from which the center of mass of a given molecule is excluded because of the presence of a second molecule. For a system of hard spheres with diameter σ it is true that

$$8\eta = \rho \frac{4\pi}{3} \sigma^3 = \rho v_{excl} \tag{3}$$

where v_{excl} denotes the excluded volume of two spheres and ρ is the particle number density $\frac{N}{V}$. The generalization of (1) to an equation of state for hard cylinders is obtained by the replacement

$$8\eta = \rho \langle v_{excl} \rangle$$

where $\langle v_{excl} \rangle$ is the expectation value of the excluded volume of two cylinders; the brackets denote a weighted average over the orientations of both cylinders. In order to obtain the expression for the hard core part of the free energy we have to integrate the thermodynamic relation $p = -(\frac{\partial F}{\partial V})_{T,N}$ and to add the term $NkT\int d\underset{\sim}{a} f(\underset{\sim}{a}) \ln 4\pi f(\underset{\sim}{a})$ because of the orientational freedom of the molecules (mixing entropy). The unit vector $\underset{\sim}{a}$ specifies the direction of a given molecule and $f(\underset{\sim}{a})$ denotes the one particle orientational distribution function. Then the hard core free energy per molecule, f_c, reads

$$\beta f_c = 3\ln\lambda + \ln\rho + \frac{3-2\tau}{(1-\tau)^2} - 4 + \int d\underset{\sim}{a} f(\underset{\sim}{a}) \ln 4\pi f(\underset{\sim}{a}) \tag{4}$$

where $\lambda = h[2\pi mkT]^{-\frac{1}{2}}$ is the socalled de Broglie wavelength with h denoting Planck's constant and m the molecular mass, $\beta = \frac{1}{kT}$, and the quantity τ is given by

$$\tau = \frac{1}{8}\rho\langle v_{excl}(\underset{\sim}{a}_{\mathcal{L}1}, \underset{\sim}{a}_{\mathcal{L}2})\rangle = \frac{1}{8}\rho\int\int d\underset{\sim}{a}_{\mathcal{L}1} d\underset{\sim}{a}_{\mathcal{L}2} f(\underset{\sim}{a}_{\mathcal{L}1}) f(\underset{\sim}{a}_{\mathcal{L}2}) v_{excl}(\underset{\sim}{a}_{\mathcal{L}1}, \underset{\sim}{a}_{\mathcal{L}2}). \qquad (5)$$

where $v_{excl}(\underset{\sim}{a}_{\mathcal{L}1}, \underset{\sim}{a}_{\mathcal{L}2})$ is the excluded volume connected with two molecules having orientations $\underset{\sim}{a}_{\mathcal{L}1}$ and $\underset{\sim}{a}_{\mathcal{L}2}$. The one-particle orientational distribution function $f(\underset{\sim}{a}_{\mathcal{L}})$ is determined selfconsistently by minimization of the free energy with respect to this function. Note that the expression for the hard core free energy reduces to the Carnahan-Starling expression for hard spheres. The long range order parameter S of the system is determined by

$$S = \int P_2(\underset{\sim}{a}_{\mathcal{L}} \cdot \underset{\sim}{n}) f(\underset{\sim}{a}_{\mathcal{L}}) d\underset{\sim}{a}_{\mathcal{L}} \qquad (6)$$

where the unit vector $\underset{\sim}{n}_{\mathcal{L}}$ (director) denotes the average orientation of the system and $P_2(z) = \frac{3}{2} z^2 - \frac{1}{2}$.

The excluded volume of two cylinders with diameter D, length L and orientations $\underset{\sim}{a}_{\mathcal{L}1}$ and $\underset{\sim}{a}_{\mathcal{L}2}$ respectively is [2]

$$v_{excl}(\underset{\sim}{a}_{\mathcal{L}1}, \underset{\sim}{a}_{\mathcal{L}2}) = 8v_o[(\frac{x}{\pi} + \frac{1}{4x})[1-(\underset{\sim}{a}_{\mathcal{L}1} \cdot \underset{\sim}{a}_{\mathcal{L}2})^2]^{\frac{1}{2}} + \frac{1}{4}(1+|\underset{\sim}{a}_{\mathcal{L}1} \cdot \underset{\sim}{a}_{\mathcal{L}2}|) + \frac{1}{\pi}E([1-(\underset{\sim}{a}_{\mathcal{L}1} \cdot \underset{\sim}{a}_{\mathcal{L}2})^2]^{\frac{1}{2}})] \qquad (7)$$

where $v_o = \frac{1}{4}\pi D^2 L$ denotes the volume of the cylinder, $x = \frac{L}{D}$, and

$$E(\sin\phi) = \int_0^{\pi/2} [1-\sin^2\phi\sin^2\psi]^{\frac{1}{2}} d\psi \qquad (8)$$

Note that the excluded volume is minimal for a length-to-breadth ratio $x = \frac{\pi}{2}$. Because expression (7) for the excluded volume is very difficult to handle exactly, two types of approximations are discussed

a) The first approximation is the usual one and is based upon an expansion in terms of Legendre polynomials. Then the expansion is broken off after the second

Legendre polynomial and the following expression results [7]

$$v_{excl}(\hat{a}_{\nu 1},\hat{a}_{\nu 2})=8v_o[\frac{\chi}{4}+\frac{\pi}{16\chi}+\frac{3}{8}+\frac{\pi}{8}-(\frac{5\pi}{128\chi}+\frac{5\chi}{32}-\frac{5(4+\pi)}{128})P_2(\hat{a}_{\nu 1}\cdot\hat{a}_{\nu 2})] \qquad (9)$$

Note that this approximation is partly incorrect. In flat contradiction with the original expression it states that the orientation dependence of the excluded volume vanishes for $\chi = \frac{\pi}{4}$ and $\chi = 1$, and the excluded volume favours a mutual perpendicular instead of parallel orientation in the intermediate region $\frac{\pi}{4} < \chi < 1$.

b) The second approximation also assumes an excluded volume of the form $v_{excl}(\hat{a}_{\nu 1},\hat{a}_{\nu 2}) = A + BP_2(\hat{a}_{\nu 1}\cdot\hat{a}_{\nu 2})$. Now, however, the coefficients A and B are calculated by the requirement that the approximate expression for the excluded volume gives the correct answer in the case that both cylinders are perpendicular or parallel to each other. Then we obtain

$$v_{excl}(\hat{a}_{\nu 1},\hat{a}_{\nu 2})=8v_o[\frac{1}{6}(\frac{4\chi}{\pi}+\frac{1}{\chi}+\frac{4}{\pi}+3)-\frac{1}{6}(\frac{4\chi}{\pi}+\frac{1}{\chi}+\frac{4}{\pi}-3)P_2(\hat{a}_{\nu 1}\cdot\hat{a}_{\nu 2})] \qquad (10)$$

Note that this approximation is minimal for a length-to-breadth ratio $\chi = \frac{\sqrt{\pi}}{2}$ just like the exact expression. Besides it has the correct behaviour for all values of χ. Unlike expression (9), however, it does not give rise to the exact value of $\langle v_{excl}\rangle$ in the isotropic phase. The relative deviation from the exact value ranges from 10% for $\chi = \frac{\sqrt{\pi}}{2}$ to 15% for both limits $\chi \to 0$ and $\chi \to \infty$.

The values of the relevant quantities at the N-I transition are calculated by solving the three equations $p_n=p_i$, $g_n=g_i$, where g denotes the Gibbs free energy per molecule, and the self-consistent equation (6) for the order parameter S. In Fig. 1 the dependence on χ of the order parameter S_{NI} at the transition is given, whereas the dependence on χ of the nematic packing fraction η_{nNI} and the relative volume change $\Delta\eta_{NI}/\eta_{iNI}$ at the transition are given in Fig. 2. The curves C_1 and C_2 in the figures refer to the approximations (9) and (10) of the excluded

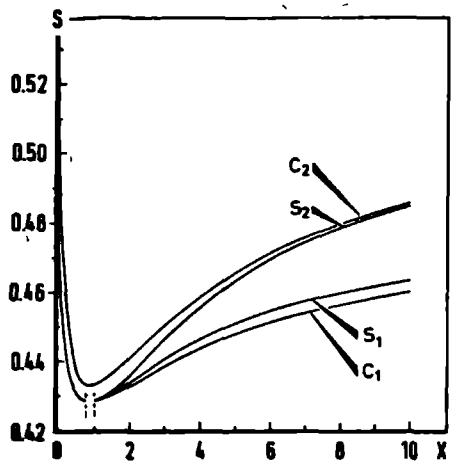

FIG. 1: The order parameter S at the N-I transition as a function of the overall length-to-breadth ratio x. The curves C_1, C_2, S_1 and S_2 refer to two different approximations of the excluded volume of hard cylinders and spherocylinders respectively. In the limit $x \to 0$, $S(C_1) \to 0.483$ and $S(C_2) \to 0.524$ whereas for $x \to \infty$, $S(C_1) = S(S_1) \to 0.483$ and $S(C_2) = S(S_2) \to 0.524$.

volume respectively. The absence of a NI-transition in a system of hard cylinders with $\frac{\pi}{4} \leq x \leq 1$ using the first approximation is, unlike remarks of Isihara [3], not surprising at all. Besides the mixing entropy the configurational or packing entropy counteracts the occurrence of the nematic phase. Obviously the results of the second approximation should be preferred. At the least this approximation describes the NI-transition in a system of hard cylinders qualitatively well. In the limit of small and large length-to-breadth ratios the predicted trends of S_{NI}, η_{nNI} and $\Delta\eta_{NI}/\eta_{iNI}$ as a function of x agree with the results of Forsyth Jr. et al. [4] obtained by using the Onsager approximation. This is not surprising, because an expansion of the free energy (4) in terms of τ and further keeping only the term linear in τ, reproduces the Onsager result.

Unfortunately a comparison with disc-like nematic liquid crystals is not possible at present due to lack of experimental data. However, it is certainly possible to test the suitability of cylinders to describe the hard core repulsive interactions in nematics like PAA. Till now spherocylinders have been used for this purpose. Therefore it is relevant to compare systems of cylinders and spherocylinders with the same length-to-breadth ratio first. The excluded volume of two spherocylinders with diameter D, overall length L + D, length-to-

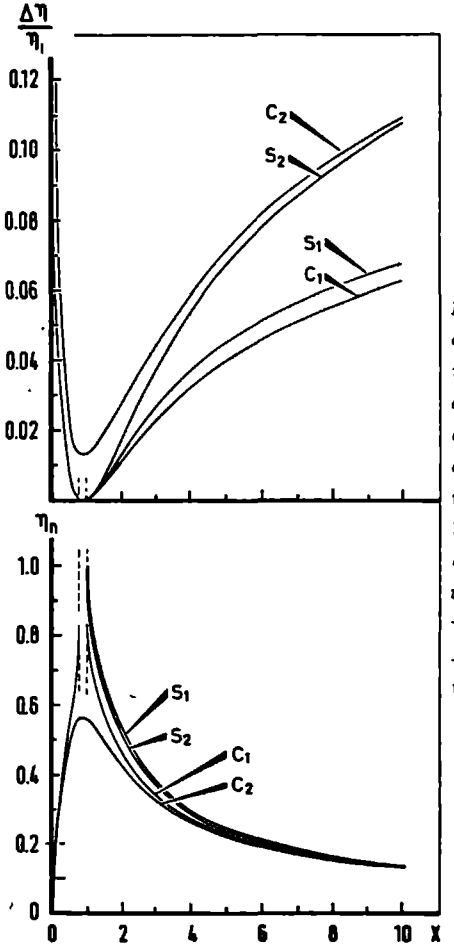

FIG. 2: The nematic packing fraction η_n and the relative volume change $\Delta\eta/\eta_i$ at the N-I transition as a function of the overall length-to-breadth ratio x. The curves C_1, C_2, S_1 and S_2 refer to two different approximations of the excluded volume of hard cylinders and spherocylinders respectively. In the limit $x \to 0$, $\Delta\eta/\eta_i(C_1) \to 0.104$ and $\Delta\eta/\eta_i(C_2) \to 0.191$ whereas for $x \to \infty$, $\Delta\eta/\eta_i(C_1) = \Delta\eta/\eta_i(S_1) \to 0.104$ and $\Delta\eta/\eta_i(C_2) = \Delta\eta/\eta_i(S_2) \to 0.191$. In the limit $x \to \infty$, $\eta_n(C_1) = \eta_n(S_1) = \eta_n(C_2) = \eta_n(S_2) \to 0$.

breadth ratio $x = \frac{L+D}{D}$, and orientations $\hat{\omega}_1$ and $\hat{\omega}_2$ has been calculated by Onsager [2]. Application of approximation (a) to this excluded volume gives

$$v_{excl}(\hat{\omega}_1,\hat{\omega}_2) = 8v_o\left[1 + \frac{3(x-1)^2}{4(3x-1)} - \frac{15(x-1)^2}{32(3x-1)} P_2(\hat{\omega}_1\cdot\hat{\omega}_2)\right] \qquad (11)$$

whereas the approximation procedure (b) gives rise to

$$v_{excl}(\hat{a}_1,\hat{a}_2)=8v_o[1+\frac{2(x-1)^2}{\pi(3x-1)}-\frac{2(x-1)^2}{\pi(3x-1)}P_2(\hat{a}_1\cdot\hat{a}_2)] \quad . \tag{12}$$

Expression (12) underestimates the exact value of $\langle v_{excl}\rangle$ in the isotropic phase, the relative deviation ranges from 0% for x=1 (spheres) to 15% for the limit $x \to \infty$. In Fig. 1 the dependence on x of the order parameter S_{NI} at the transition is given, whereas the dependence on x of the nematic packing fraction η_{nNI} and the relative volume change $\Delta\eta_{NI}/\eta_{iNI}$ at the transition are given in Fig. 2. The symbols S_1 and S_2 refer to the approximations (11) and (12) of the excluded volume respectively. Clearly both approximations of the excluded volume result here in the same qualitative description of the behaviour of a system of spherocylinders.

In order to describe the intermolecular attractions in the nematic phase we assume further, analogous to Cotter and Ypma et al. [8,9], that each molecule moves about in an effective mean field described by the pseudo potential

$$u(\hat{a}\cdot\hat{n}) = -\rho J_0 - \rho J_2 S P_2(\hat{a}\cdot\hat{n}) \tag{13}$$

Then the Helmholtz free energy reads

$$f = f_c - \tfrac{1}{2}J_0\rho^2 - \tfrac{1}{2}J_2\rho^2S^2 \tag{14}$$

where f_c is given by expression (4). In order to describe PAA we determine the parameters J_0, J_2 and x such that the experimental values of the quantities T_{NI}, η_{nNI} and $\Gamma(T_{NI})$ at a constant pressure of one atmosphere are approximately reproduced, where we use Vieillard-Baron's value for v_o [10]. $\Gamma(T)$ is defined by

$$\Gamma(T) = \frac{V(\partial S/\partial V)_T}{T(\partial S/\partial T)_V} = \frac{\eta}{T}\left(\frac{\partial T}{\partial \eta}\right)_S, \tag{15}$$

it indicates the relative importance of temperature and volume changes in affecting the nematic order. In Table I the results of our calculations are given

TABLE I: Comparison between the N-I transition in the model systems of hard cylinders and hard spherocylinders and PAA. $\frac{\Delta\Sigma}{Nk}$ *is the transition entropy.*

Parameter	Cylinders	Spherocylinders	
x	$\sqrt{\pi}/2$	1.33	
J_0/kv_o	22758°K	46563°K	
J_2/kv_o	2253°K	1974°K	
Quantity			PAA
T_{NI}	409.0°K	409.0°K	409°K[11]
S_{NI}	0.539	0.454	0.40[11]
η_{nNI}	0.478	0.620	0.62[10,11]
$\Delta\eta_{NI}/\eta_{iNI}$	0.0465	0.0077	0.0035[11]
$\Delta\Sigma/Nk$	0.973	0.577	0.17[12]
$\Gamma(T_{NI})$	4.00	3.99	4.0[13]
$(\frac{dT_{NI}}{dp})_{p=1atm}$	166.9°K/kbar	35.7°K/kbar	48°K/kbar[14]

concerning model systems consisting of cylinders and spherocylinders together with the experimental results for PAA. The pressure depence of the transition temperature, $\frac{dT_{NI}}{dp}$, is determined by Clausius-Clapeyron's law. Note that the best fit for cylinders is obtained with $x = \frac{\sqrt{\pi}}{2}$, i.e. with minimal excluded volume. Clearly a spherocylindrical hard core gives rise to a much better description of PAA than a cylindrical hard core, at least within the present approximations. This conclusion holds for widely studied nematics like MBBA, APAPA, MBCA etc. as well.

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CHAPTER V

ELASTIC CONSTANTS OF NEMATIC AND CHOLESTERIC LIQUID CRYSTALS AND TENSOR FIELDS

1. Introduction

The continuum theory of Oseen[1] and Frank[2] describes liquid crystals in terms of a vector field $\vec{n}(\vec{r})$. Here the unit vector $\vec{n}(\vec{r})$ specifies the local orientation of the anisotropic material at the site $\vec{r}$. Starting point is a perfectly aligned situation, i.e. $\vec{n}(\vec{r})$ does not depend on $\vec{r}$. The continuum theory then deals with small deviations of this state, i.e. only first and second order derivatives of $\vec{n}(\vec{r})$ are taken into account in the expression for the free energy density $f(\vec{r})$. Clearly $f(\vec{r})$ is a scalar field and can be expressed like

$$f(\vec{r}) = f_0 + K_{\alpha\beta}(\vec{r})\partial_\alpha n_\beta(\vec{r}) + K_{\alpha\beta\gamma\delta}(\vec{r})\left[\partial_\alpha n_\beta(\vec{r})\right]\left[\partial_\gamma n_\delta(\vec{r})\right] + K_{\alpha\beta\gamma}(\vec{r})\partial_\alpha\partial_\beta n_\gamma(\vec{r}) \qquad (1.1)$$

where f_0 denotes the free energy of the non-distorted state, $\alpha, \beta, \gamma, \delta = x, y, z$, $\partial_\alpha n_\beta(\vec{r}) = (\partial n_\beta(\vec{r}))/\partial\alpha$ and the Einstein summation convention is used. As shown by Frank this expression reduces to

$$f(\vec{r}) = f_0 + \frac{1}{2}\left[\frac{4\pi}{p}K_t(\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r})) + K_s(\vec{\nabla}\cdot\vec{n}(\vec{r}))^2 + K_t(\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 + K_b(\vec{n}(\vec{r})\wedge\vec{\nabla}\wedge\vec{n}(\vec{r}))^2\right] \qquad (1.2)$$

where K_s, K_t and K_b denote the elastic constants for splay, twist and bend respectively and p is the natural pitch of the material ($\frac{2\pi}{p} = 0$ for a nematic). Frank obtained this result by introducing a local coordinate system at an arbitrary point with its z-axis parallel to the director at that point and assuming both uniaxial symmetry around the local z-axis and the absence of physical polarity. Recasting his result in rotationally invariant form and omitting the surface terms he arrived at expression (1.2) for $f(\vec{r})$.

The purpose of this chapter is twofold. Because the appropriate mathematical tool for dealing with expressions like (1.1) is tensor analysis, we present

first a simple derivation of the distortion free energy density in terms of that formalism. Next we calculate the elastic constants of a number of molecular models, like e.g. the Maier-Saupe model[3], by conceiving these models as tensor fields. In this way we do not have to resort to the introduction of distorting fields as proposed by Priest[4], but arrive at these constants in a natural way, i.e. as indicated by the continuum theory.

II. Derivation

The relevant symmetries are the rotational invariance of the free energy density $f(\vec{r})$ and its invariance for replacing $\vec{n}(\vec{r})$ by $-\vec{n}(\vec{r})$. Consequently, the coefficients $K_{\alpha\beta}(\vec{r})$, $K_{\alpha\beta\gamma\delta}(\vec{r})$ and $K_{\alpha\beta\gamma}(\vec{r})$ must have the following transformational character.

(1) $K_{\alpha\beta}(\vec{r})$ transforms like $K_1\epsilon_{\alpha\beta\gamma}n_\gamma(\vec{r})$, where K_1 is an arbitrary constant and $\epsilon_{\alpha\beta\gamma}$ denotes the well-known Levi-Civita tensor.

(2) $K_{\alpha\beta\gamma\delta}(\vec{r})$ transforms according to one of the following ten ways $K_2n_\alpha(\vec{r})n_\beta(\vec{r})n_\gamma(\vec{r})n_\delta(\vec{r})$, $K_3\delta_{\alpha\beta}n_\gamma(\vec{r})n_\delta(\vec{r})$, $K_4\delta_{\alpha\gamma}n_\beta(\vec{r})n_\delta(\vec{r})$, $K_5\delta_{\alpha\delta}n_\beta(\vec{r})n_\gamma(\vec{r})$, $K_6\delta_{\beta\gamma}n_\alpha(\vec{r})n_\delta(\vec{r})$, $K_7\delta_{\beta\delta}n_\alpha(\vec{r})n_\gamma(\vec{r})$, $K_8\delta_{\gamma\delta}n_\alpha(\vec{r})n_\beta(\vec{r})$, $K_9\delta_{\alpha\beta}\delta_{\gamma\delta}$, $K_{10}\delta_{\alpha\gamma}\delta_{\beta\delta}$, and $K_{11}\delta_{\alpha\delta}\delta_{\beta\gamma}$, where $\delta_{\alpha\beta}$ denotes the well-known Kronecker tensor and K_i, $i = 2,3,\ldots,11$, are arbitrary constants.

(3) $K_{\alpha\beta\gamma}(\vec{r})$ transforms according to one of the following four ways $K_{12}n_\alpha(\vec{r})n_\beta(\vec{r})n_\gamma(\vec{r})$, $K_{13}\delta_{\alpha\beta}n_\gamma(\vec{r})$, $K_{14}\delta_{\alpha\gamma}n_\beta(\vec{r})$ and $K_{15}\delta_{\beta\gamma}n_\alpha(\vec{r})$, where K_i, $i = 12,13,14,15$, are arbitrary constants.

It is easily checked that this list is exhaustive.

Neglecting the contribution to the surface energy, i.e. the terms giving rise to $\int \partial_\alpha u_\alpha(\vec{r})\,d\vec{r}$, where $\vec{u}(\vec{r})$ is an arbitrary vector, are neglected on account of Gauss's theorem, and further using the fact that $\vec{n}(\vec{r})$ is a unit vector, i.e. $n_\beta(\vec{r})n_\beta(\vec{r}) = 1$ or $\partial_\alpha\left[n_\beta(\vec{r})n_\beta(\vec{r})\right] = 2n_\beta(\vec{r})\partial_\alpha n_\beta(\vec{r}) = 0$, we arrive at

$$f(\vec{r}) = f_0 + K_1\varepsilon_{\alpha\beta\gamma}n_\gamma(\vec{r})\partial_\alpha n_\beta(\vec{r}) + (K_7-K_{12})n_\alpha(\vec{r})n_\beta(\vec{r})\left[\partial_\alpha n_\gamma(\vec{r})\right]\left[\partial_\beta n_\gamma(\vec{r})\right]$$
$$+ (K_{10}-K_{13})\left[\partial_\alpha n_\beta(\vec{r})\right]\left[\partial_\alpha n_\beta(\vec{r})\right] + (K_9+K_{11}-K_{14}-K_{15})\left[\partial_\alpha n_\alpha(\vec{r})\right]\left[\partial_\beta n_\beta(\vec{r})\right] \quad (2.1)$$

Clearly a number of invariant terms do not contribute, e.g.

$$K_2\delta_{\alpha\beta}n_\gamma(\vec{r})n_\delta(\vec{r})\left[\partial_\alpha n_\beta(\vec{r})\right]\left[\partial_\gamma n_\delta(\vec{r})\right] = \tfrac{1}{2}K_2 n_\gamma(\vec{r})\left[\partial_\alpha n_\alpha(\vec{r})\right]\left[n_\delta(\vec{r})\partial_\gamma n_\delta(\vec{r})\right] = 0 \quad (2.2)$$

and the remaining terms can be rewritten in one of the four invariant forms appearing in expression (2.1), e.g.

$$K_{12}n_\alpha(\vec{r})n_\beta(\vec{r})n_\gamma(\vec{r})\partial_\alpha\partial_\beta n_\gamma(\vec{r}) = K_{12}n_\alpha(\vec{r})n_\beta(\vec{r})\partial_\alpha\left[n_\gamma(\vec{r})\partial_\beta n_\gamma(\vec{r})\right]$$
$$- K_{12}n_\alpha(\vec{r})n_\beta(\vec{r})\left[\partial_\alpha n_\gamma(\vec{r})\right]\left[\partial_\beta n_\gamma(\vec{r})\right]$$
$$= - K_{12}n_\alpha(\vec{r})n_\beta(\vec{r})\left[\partial_\alpha n_\gamma(\vec{r})\right]\left[\partial_\beta n_\gamma(\vec{r})\right] \quad (2.3)$$

In order to obtain the Frank expression (1.2) for the distortion free energy density we have to rewrite the invariants appearing in expression (2.1) in terms of the invariants appearing in expression (1.2). It is easily verified (see also the Appendix) that

$$\varepsilon_{\alpha\beta\gamma}n_\gamma(\vec{r})\partial_\alpha n_\beta(\vec{r}) = \vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r}) \quad (2.4a)$$

$$n_\alpha(\vec{r})n_\beta(\vec{r})\left[\partial_\alpha n_\gamma(\vec{r})\right]\left[\partial_\beta n_\gamma(\vec{r})\right] = (\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 - (\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 = (\vec{n}(\vec{r})\wedge\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 \quad (2.4b)$$

$$\left[\partial_\alpha n_\beta(\vec{r})\right]\left[\partial_\alpha n_\beta(\vec{r})\right] = (\vec{\nabla}\cdot\vec{n}(\vec{r}))^2 + (\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 + (\vec{n}(\vec{r})\wedge\vec{\nabla}\wedge\vec{n}(\vec{r}))^2 \quad (2.4c)$$

$$\left[\partial_\alpha n_\alpha(\vec{r})\right]\left[\partial_\beta n_\beta(\vec{r})\right] = (\vec{\nabla}\cdot\vec{n}(\vec{r}))^2 \quad (2.4d)$$

Using the identities (2.4) we obtain the Frank distortion free energy density with elastic constants

$$K_s = 2\left[K_9 + K_{10} + K_{11} - K_{13} - K_{14} - K_{15}\right] \quad (2.5a)$$

$$K_t = 2\left[K_{10} - K_{13}\right] \quad (2.5b)$$

$$K_b = 2\left[K_7 + K_{10} - K_{12} - K_{13}\right] \quad (2.5c)$$

and a pitch

$$p = \left[\frac{4\pi(K_{10}-K_{13})}{K_1}\right]^{-1} \tag{2.5d}$$

Obviously the constant K_i, $i = 2,\ldots,15$, are such that K_s, K_t and K_b are positive.

III. Elastic constants of molecular models

The elastic constants of a number of molecular models can be easily calculated by conceiving these models as tensor fields. As a first example we consider the well-known Maier-Saupe model

$$-\frac{1}{2}\sum_{i,j} J_{ij}(\vec{n}_i\cdot\vec{n}_j)^2 \tag{3.1}$$

where the unit vector $\vec{n}_i$ specifies the orientation of molecule i situated at site $\vec{r}_i$. The coupling constant J_{ij} depends on the distance $|\vec{r}_i-\vec{r}_j|$ between the molecules i and j. Next we introduce the field $\vec{n}(\vec{r})$ defined by $\vec{n}(\vec{r}_i) = \vec{n}_i$. Assuming a uniform distribution of the molecules this model gives rise to the following free energy density

$$f(\vec{r}) = -\frac{1}{2}\rho^2\int J(\varepsilon)\left[\vec{n}(\vec{r})\cdot\vec{n}(\vec{r}+\vec{\varepsilon})\right]^2 d\vec{\varepsilon} \tag{3.2}$$

where ρ denotes the density of the system, $\varepsilon = |\vec{\varepsilon}|$ and the integration is taken over the total volume of the system. In order to obtain the elastic constants we expand the free energy density (3.2) around its equilibrium value

$$\begin{aligned} f(\vec{r}) &= -\frac{1}{2}\rho^2\int J(\varepsilon)\left[n_\alpha(\vec{r})\{n_\alpha(\vec{r}) + \varepsilon_\beta\partial_\beta n_\alpha(\vec{r}) + \frac{1}{2}\varepsilon_\beta\varepsilon_\gamma\partial_\beta\partial_\gamma n_\alpha(\vec{r}) + ..\}\right] \\ &\quad\times\left[n_\mu(\vec{r})\{n_\mu(\vec{r}) + \varepsilon_\nu\partial_\nu n_\mu(\vec{r}) + \frac{1}{2}\varepsilon_\nu\varepsilon_\rho\partial_\nu\partial_\rho n_\mu(\vec{r}) + ..\}\right] d\vec{\varepsilon} \\ &= f_0 - \frac{1}{2}\rho^2\int J(\varepsilon)\varepsilon_\beta\varepsilon_\gamma d\vec{\varepsilon}\, n_\alpha(\vec{r})\partial_\beta\partial_\gamma n_\alpha(\vec{r}) + \ldots \end{aligned} \tag{3.3}$$

where the free energy density f_0 of the equilibrium state is given by

$$f_0 = -\frac{1}{2}\rho^2\int J(\varepsilon)\left[\vec{n}(\vec{r})\cdot\vec{n}(\vec{r})\right]^2 d\vec{\varepsilon} = -2\pi\rho^2\int J(\varepsilon)\,\varepsilon^2\,d\varepsilon \tag{3.4}$$

Using

$$\int J(\varepsilon)\,\varepsilon_\beta\varepsilon_\gamma\,d\vec{\varepsilon} = \delta_{\beta\gamma}\int J(\varepsilon)\,\varepsilon_z^2\,d\vec{\varepsilon} = \frac{4\pi}{3}\delta_{\beta\gamma}\int J(\varepsilon)\,\varepsilon^4\,d\varepsilon \tag{3.5}$$

and relation (2.4c) we arrive at

$$f(\vec{r}) = f_0 + \frac{2\pi}{3}\rho^2\int J(\varepsilon)\varepsilon^4 d\varepsilon\left[(\vec{\nabla}\cdot\vec{n}(\vec{r}))^2+(\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r}))^2+(\vec{n}(\vec{r})\wedge\vec{\nabla}\wedge\vec{n}(\vec{r}))^2\right] \tag{3.6}$$

i.e.

$$K_s = K_t = K_b = \frac{4\pi}{3}\rho^2\int J(\varepsilon)\,\varepsilon^4\,d\varepsilon \tag{3.7}$$

Next we calculate the elastic constants of a molecular model for the cholesteric phase. The discussed model consists of two interactions, namely the Maier-Saupe interaction and a twist interaction[5]

$$-\frac{1}{2}\sum_{i,j} A_{ij}(\vec{n}_i\cdot\vec{n}_j)(\vec{n}_i\wedge\vec{n}_j\vec{u}_{ij}) \tag{3.8}$$

where $\vec{u}_{ij}$ is a unit vector pointing from the center of molecule i towards that of j. Assuming a uniform distribution of the molecules the twist interaction can be represented by the following tensor field

$$-\frac{1}{2}\rho^2\int\frac{A(\varepsilon)}{\varepsilon}\left[\vec{n}(\vec{r})\vec{n}(\vec{r}+\vec{\varepsilon})\right]\left[\vec{n}(\vec{r})\wedge\vec{n}(\vec{r}+\vec{\varepsilon})\cdot\vec{\varepsilon}\right]d\vec{\varepsilon} \tag{3.9}$$

In order to calculate the contribution to the distortion free energy density we expand this tensor field around the perfectly aligned state. Then we obtain

$$\frac{2\pi}{3}\rho^2\int A(\varepsilon)\,\varepsilon\,d\varepsilon\left[\vec{n}(\vec{r})\cdot\vec{\nabla}\wedge\vec{n}(\vec{r})\right] . \tag{3.10}$$

The contribution of the twist interaction to the splay, twist and bend elastic constants is zero.

Finally we give the elastic constants of a number of molecular models of the form

$$-\frac{1}{2}\sum_{i,j} J_{ij}^{uvw}\left[\vec{n}_i\cdot\vec{u}_{ij}\right]^u\left[\vec{n}_j\cdot\vec{u}_{ij}\right]^v\left[\vec{n}_i\cdot\vec{n}_j\right]^w \tag{3.11}$$

where u, v and w are such that the expression is invariant for replacing $\vec{n}_i$ by $-\vec{n}_i$ and/or $\vec{n}_j$ by $-\vec{n}_j$, i.e. both u+w and v+w are even, and the coupling constants J_{ij}^{uvw} depend on $|\vec{r}_i-\vec{r}_j|$. The fact that the coupling constants can only depend on $|\vec{r}_i-\vec{r}_j|$ and not on the direction of $\vec{r}_i-\vec{r}_j$ is dictated by the rotational invariance of the interactions (3.11). It should be remarked here that any interaction, which is invariant for replacing $\vec{n}$ by $-\vec{n}$ and for changing the handedness of the coordinate system, can be expanded in terms of these types of interactions. Assuming a uniform distribution of the molecules and representing the molecular models by the corresponding tensor fields the elastic constants can be easily calculated. The results for the molecular models with $u + v + w \leq 5$ are given in the table where we have expressed the elastic constants in units of $\frac{4\pi}{3}\rho^2\int J^{uvw}(\varepsilon)\,\varepsilon^4\,d\varepsilon$. Because of symmetry an interchange of u and v does not affect the values of the elastic constants.

TABLE: The elastic constants of the molecular models (3.11) with $u+v+w \leq 5$ in units of $\frac{4\pi}{3}\rho^2\int J^{uvw}(\varepsilon)\,\varepsilon^4\,d\varepsilon$.

u	v	w	K_s	K_t	K_b
2	0	0	0	0	0
0	0	2	1	1	1
1	1	1	$\frac{2}{5}$	$\frac{1}{5}$	$\frac{2}{5}$
4	0	0	0	0	0
0	0	4	2	2	2
2	2	0	$\frac{6}{35}$	$\frac{2}{35}$	$\frac{6}{35}$
2	0	2	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{3}{5}$
3	1	1	$\frac{6}{35}$	$\frac{3}{35}$	$\frac{12}{35}$
1	1	3	$\frac{3}{5}$	$\frac{2}{5}$	1

As easily can be deduced from this table the ratio between the elastic constants in the original induced dipole-dipole interaction model of Maier and Saupe[6] is given by $K_s : K_t : K_b = 5 : 11 : 5$.

Appendix

Using the fact that $\vec{n}$ is a unit vector and neglecting surface terms we have

$$(\vec{n}\cdot\vec{\nabla}\wedge\vec{n})^2 = n_\alpha\varepsilon_{\alpha\beta\gamma}[\partial_\beta n_\gamma]n_\mu\varepsilon_{\mu\nu\rho}[\partial_\nu n_\rho] = (\delta_{\alpha\mu}\delta_{\beta\nu}\delta_{\gamma\rho} + \delta_{\beta\mu}\delta_{\gamma\nu}\delta_{\alpha\rho} + \delta_{\gamma\mu}\delta_{\alpha\nu}\delta_{\beta\rho}$$
$$- \delta_{\alpha\mu}\delta_{\gamma\nu}\delta_{\beta\rho} - \delta_{\gamma\mu}\delta_{\beta\nu}\delta_{\alpha\rho} - \delta_{\beta\mu}\delta_{\alpha\nu}\delta_{\gamma\rho})n_\alpha[\partial_\beta n_\gamma]n_\mu[\partial_\nu n_\rho] =$$
$$= [\partial_\alpha n_\beta][\partial_\alpha n_\beta] - [\partial_\alpha n_\alpha][\partial_\beta n_\beta] - n_\alpha n_\beta[\partial_\alpha n_\gamma][\partial_\beta n_\gamma] \qquad (A1)$$

and

$$(\vec{\nabla}\wedge\vec{n})^2 = \varepsilon_{\alpha\beta\gamma}[\partial_\beta n_\gamma]\varepsilon_{\alpha\mu\nu}[\partial_\mu n_\nu] = [\partial_\alpha n_\beta][\partial_\alpha n_\beta] - [\partial_\alpha n_\alpha][\partial_\beta n_\beta] \qquad (A2)$$

Hence

$$n_\alpha n_\beta[\partial_\alpha n_\gamma][\partial_\beta n_\gamma] = (\vec{\nabla}\wedge\vec{n})^2 - (\vec{n}\cdot\vec{\nabla}\wedge\vec{n})^2 = (\vec{n}\wedge\vec{\nabla}\wedge\vec{n})^2 \qquad (A3)$$

and

$$[\partial_\alpha n_\beta][\partial_\alpha n_\beta] = (\vec{\nabla}\wedge\vec{n})^2 + (\vec{\nabla}\cdot\vec{n})^2 = (\vec{n}\wedge\mathrm{rot}\vec{n})^2 + (\vec{n}\cdot\mathrm{rot}\vec{n})^2 + (\vec{\nabla}\cdot\vec{n})^2 \qquad (A4)$$

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CHAPTER VI

ON THE ELASTIC CONSTANTS OF NEMATICS; A COMPARISON BETWEEN EXPERIMENT AND MOLECULAR THEORY

Purpose of this chapter is to investigate the adequacy of present molecular statistical theories [1,2] for an understanding of the experimental behaviour of the elastic constants of nematics. Summarizing it can be said that these theories, which are based upon the assumption that a truncated expansion of the intermolecular repulsive and attractive interactions in terms of spherical harmonics is relevant, give rise to the following expressions for the elastic constants

$$K_{11} = \bar{K}(1 + \Delta - 3\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}) \tag{1}$$

$$K_{22} = \bar{K}(1 - 2\Delta - \Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}) \tag{2}$$

$$K_{33} = \bar{K}(1 + \Delta + 4\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}) \tag{3}$$

where the constants K_{11}, K_{22} and K_{33} are associated with splay, twist and bend respectively, $3\bar{K} = K_{11}+K_{22}+K_{33}$, and $\langle P_n \rangle$ denotes the expectation value of the n-th order Legendre polynomial. The quantities Δ and Δ' can be approximately written as

$$\Delta = \frac{c + dT}{a + bT} \tag{4}$$

$$\Delta' = \frac{e + fT}{a + bT} \tag{5}$$

where T denotes the temperature. The constants a, c and e describe the attractive intermolecular interactions, whereas the constants b, d and f represent the repulsive intermolecular interactions. The expression for $\bar{K}$ reads

$$\bar{K} = \tfrac{1}{2}\rho^2 \langle P_2 \rangle^2 (a + bT) \tag{6}$$

where ρ denotes the particle number density $\frac{N}{V}$. For a system of hard spherocylinders, i.e. $\alpha=\sigma=\varepsilon=0$, Priest showed

$$\frac{d}{b} = \frac{2R^2-2}{7R^2+20} \tag{7}$$

$$\frac{f}{b} = \frac{9(3R^2-8)}{16(7R^2+20)} \tag{8}$$

$$b = \frac{5\pi}{672} B^5(7R^4+20R^2) \tag{9}$$

with $R = \frac{L}{B}$, where B and L+B denote the breadth and the length of a spherocylinder respectively.

In order to analyse the relevant theoretical expressions the temperature dependence of the six quantities K_{11}, K_{22}, K_{33}, ρ, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ has to be known experimentally. At present these six quantities have only been measured for MBBA and 5CB [3,4,5,6] as far as we know. In both substances $\langle P_4 \rangle$ changes sign near the clearing point, whereas K_{33} remains larger than K_{11}. According to eqs. (1)-(3), however, the bend and splay elastic constants are equal at the temperature, where $\langle P_4 \rangle$ changes sign. Clearly experiment and theory are in flat contradiction for these materials.

In a number of nematics, e.g. HNBP [7] and BBOA [3,8], the order parameter $\langle P_4 \rangle$ does not change sign as a function of temperature. Unfortunately these nematics cannot be used for our analysis because of lack of experimental data of their elastic constants and densities. In other nematogens like MBCA and the homologues of APAPA, which will be denoted by APAPAn, where n denotes the number of carbon atoms of the alkyl chain, $\langle P_4 \rangle$ has not been measured. Obviously experiment and theory contradict each other if $\langle P_4 \rangle$ changes sign as a function of temperature in the nematic region of MBCA and APAPAn, because either K_{33} is larger than K_{11} or K_{11} is larger than K_{33} for these materials [5]. Therefore let us assume that $\langle P_4 \rangle$ does not change sign in MBCA and APAPAn and then find out whether the expressions (1)-(9) have any significance.

In Fig. 1 the observed dependence on the reduced temperature of the quantity $2\rho^{-2}\langle P_2\rangle^{-2}\bar{K}$ is shown up to $\frac{T}{T_{NI}} = 0.995$ for MBBA, OHMBBA, MBCA and the homologues APAPAn (n=1-5,9). Generally the errors in the experimental data are about 5%, but they increase quite near the nematic-isotropic transition temperature T_{NI}.

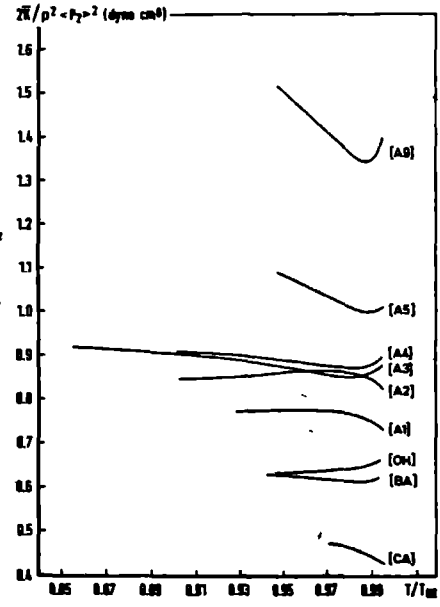

FIG. 1: The observed reduced temperature dependence of $2\rho^{-2}\langle P_2\rangle^{-2}\bar{K}$ for the homologues APAPAn (n=1-5,9) [An], MBBA [BA], MBCA [CA] and OHMBBA [OH]. The data are taken from Leenhouts [5].

The data have been taken from Leenhouts [5]. It is clear that a trend for the quantity $2\rho^{-2}\langle P_2\rangle^{-2}\bar{K}$ within the homologous series of APAPA is indicated in Fig. 1. The results of a least square fit for the constants a and b appearing in expression (6) are given in Table I. The observed and fitted reduced temperature dependences agree within 2% except in the region $0.99 < \frac{T}{T_{NI}} < 0.995$, where the deviation between the observed and fitted data is slightly larger. The largest deviation concerns APAPA3 being 5% at $\frac{T}{T_{NI}} = 0.995$. Taking into account the

TABLE I: Values of the parameters a and b giving rise to the best fit of the curves shown in Fig. 1.

Substance	a(dyne cm^6)	$b(10^{-4}$dyne cm^6 K^{-1})	$\frac{b}{a}(10^{-4}$K^{-1})
MBCA	2.276	-47	-21
APAPA	1.118	-9	-8
APAPA3	1.279	-11	-9
APAPA5	2.992	-54	-18
APAPA9	4.782	-94	-20
APAPA2	0.865	-0.3	-0.4
APAPA4	1.241	-10	-8

experimental errors it may be stated that the agreement between expression (6) and experiment is quite satisfactory. Although the values for b are small, the influence of b is considerable, because bT_{NI} and a are of the same magnitude. Table I shows clearly the importance of attractive interactions in order to describe these nematics. According to this table an even-odd effect for $\frac{b}{a}$ exists within the homologues of APAPA. An insurmountable problem, however, concerns the negative sign of b. Hard core repulsions give rise to a positive b, see e.g. expression (9). Thus the molecular statistical expression (6) looses its physical meaning.

This conclusion is further sustained by calculating the quantities Δ and $\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}$ for MBCA and the homologues APAPAn (n=1-5,9) using the experimental data of the elastic constants and the expressions (1)-(3). The resulting dependences of Δ and $\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}$ on the reduced temperature are shown in Fig. 2 and Fig. 3 respectively. For APAPA9 the quantity $\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}$ is negative, because K_{11} is larger than K_{33} in this material. Clearly both Δ and $\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle}$ are temperature

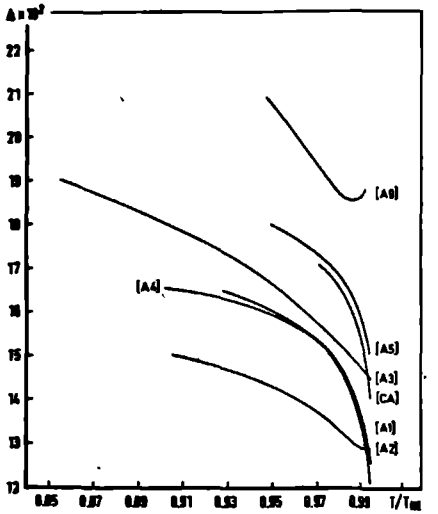

FIG. 2: The reduced temperature dependence of the quantity Δ, for the homologues APAPAn (n=1-5,9) [An] and for MBCA [CA].

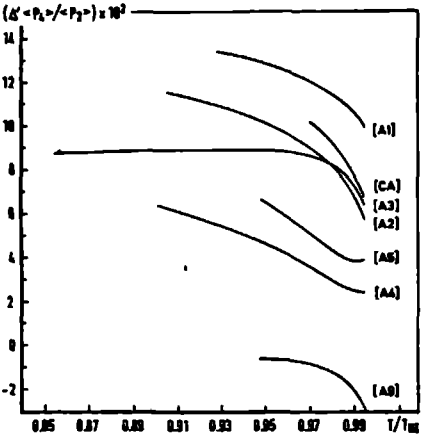

FIG. 3: The reduced temperature dependence of the quantity $\Delta' \frac{\langle P_4 \rangle}{\langle P_2 \rangle^2}$ for the homologues APAPAn (n=1-5,9) [An] and for MBCA [CA].

dependent. For a further comparison with theory we have to investigate whether these curves can be fitted with the expressions (4) and (5). Because $\langle P_4 \rangle$ is unknown we can only investigate expression (4). The results of a least square fit for the constants c and d appearing in expression (4) are given in Table II, where we used the values of a and b as given in Table I. The observed and fitted reduced temperature dependences agree within 4% if $\frac{T}{T_{NI}} \leq 0.99$. In the region $0.99 < \frac{T}{T_{NI}} < 0.995$ the deviations between the observed and fitted reduced temperature dependences of Δ increase till 6% except in the cases of APAPA and APAPA4, where the deviations increase till 10% and 15% respectively. The experimental errors for K_{11} and K_{22} are less than 4%, whereas those for K_{33} do not exceed 6%. Therefore the fit procedure is not entirely satisfactory for some of the nematics in question. A second fit procedure is to treat a and b as

TABLE II: Values of the parameters c and d giving rise to the best fit of the observed temperature dependence of the quantity Δ, using the parameters a and b given in Table I.

Substance	c(dyne cm^6)	$d(10^{-4}$dyne cm^{6}K$^{-1})$	$\frac{c}{a}$	$\frac{d}{a}(10^{-4}$K$^{-1})$
MBCA	0.864	-21	0.380	-9
APAPA	0.529	-11	0.473	-10
APAPA3	0.478	-9	0.374	-7
APAPA5	1.081	-25	0.361	-8
APAPA9	1.584	-36	0.331	-8
APAPA2	0.324	-6	0.375	-6
APAPA4	0.491	-10	0.395	-8

free parameters as well. In this way we get an idea about the internal consistency of the theory. The results of a least square fit for $\frac{b}{a}$, $\frac{c}{a}$ and $\frac{d}{a}$ are given in Table III. With the exception of APAPA9 the observed and fitted reduced temperature dependences agree now within 1% up to $\frac{T}{T_{NI}} = 0.995$. In the case of APAPA9 the first fit procedure appears to be superior. A comparison between the values

TABLE III: Values of the relative parameters $\frac{b}{a}$, $\frac{c}{a}$ and $\frac{d}{a}$ giving rise to the best fit of the observed temperature dependence of the quantity Δ.

Substance	$\frac{b}{a}(10^{-4}$K$^{-1})$	$\frac{c}{a}$	$\frac{d}{a}(10^{-4}$K$^{-1})$
MBCA	-25	0.184	-5
APAPA	-26	0.174	-4
APAPA3	-23	0.225	-5
APAPA5	-26	0.192	-5
APAPA2	-24	0.170	-4
APAPA4	-27	0.171	-5

of $\frac{b}{a}$, $\frac{c}{a}$ and $\frac{d}{a}$ given in the Tables I and II and those given in Table III indicates clearly that the expressions (4) and (6) are incompatible.

The conclusion of this analysis is rather disappointing. An adequate interpretation of the experimental behaviour of the elastic constants of nematics is not possible using the available truncated theoretical expressions.

This conclusion is sustained by related work of Karat et al. [9]. It should be remarked, however, that our point of view differs from that taken by Karat et al..

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SAMENVATTING

Dit proefschrift handelt over de toestandsvergelijking voor en de elastische constanten van nematische vloeibare kristallen (nematica). Nematica zijn opgebouwd uit langwerpige organische moleculen. Deze moleculen kunnen aanleiding geven tot één of meer extra fasen gelegen tussen de vaste en de isotrope vloeistof fase. Deze tussenliggende fasen zijn de vloeibare kristallijne fasen. In de nematische fase zijn de zwaartepunten van de moleculen verdeeld als in een vloeistof, maar de lange assen van de moleculen wijzen gemiddeld in één bepaalde richting. Meer algemene informatie over vloeibare kristallen, en nematica in het bijzonder, wordt gegeven in hoofdstuk I.

De hoofdstukken II, III en IV gaan over de toestandsvergelijking voor nematica. In hoofdstuk II wordt een eenvoudige fenomenologische afleiding van deze toestandsvergelijking gegeven, waarbij de moleculen beschreven worden d.m.v. harde staven. Voor sferocylinders (dit zijn cylinders die aan beide uiteinden begrensd worden door halve bollen) wordt een kwantitatieve vergelijking met bestaande toestandsvergelijkingen gemaakt.

In hoofdstuk III worden zowel afstotende als aantrekkende krachten tussen de moleculen in rekening gebracht. De interacties worden daarbij behandeld in de moleculaire veld benadering. Het thermodynamisch gedrag van dit modelsysteem wordt vergeleken met de experimentele gegevens voor een aantal thermotrope nematica, waaronder twee homologe reeksen. Voor alle beschouwde nematica kan een kwantitatieve overeenstemming tussen theorie en experiment verkregen worden. In het algemeen wordt echter nog geen kwantitatieve of fysisch bevredigende beschrijving van de onderlinge verschillen tussen de diverse nematica verkregen.

Naast nematica opgebouwd uit langwerpige moleculen, zijn er recentelijk ook nematica gevonden bestaande uit moleculen met een schijfvormige structuur. Beide molecuulvormen kunnen, in eerste orde, benaderd worden door

cylinders van verschillende hoogte. In hoofdstuk IV wordt een toestandsvergelijking voor cylindervormige moleculen gegeven.

De laatste twee hoofdstukken van dit proefschrift betreffen deformaties binnen de nematische en cholesterische fase. (De laatste fase is in feite een spontaan vervormde nematische fase). Deze vervormingen spelen een belangrijke rol in praktische toepassingen van vloeibare kristallen, bijv. displays. Er zijn drie basisvervormingen: splay, bend en twist. De bijbehorende elastische constanten geeft men aan met K_s, K_t en K_b. In hoofdstuk V wordt de uitdrukking voor de toename van de vrije energiedichtheid van een nematisch en cholesterisch medium t.g.v. de verschillende vervormingen afgeleid m.b.v. tensoranalyse. Verder worden in dit hoofdstuk de onderlinge verhoudingen van K_s, K_t en K_b berekend voor een aantal intermoleculaire interacties waarbij het vloeibare kristal als een tensorveld wordt behandeld. Tenslotte wordt in hoofdstuk VI de temperatuurafhankelijkheid van de drie elastische constanten, zoals gegeven door een aantal moleculair statistische theorieën vergeleken met het experiment.

Curriculum Vitae

van

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STELLINGEN

I

Aangezien een biologisch gevormd mengsel van aminozuren en suikers geen draaiing van de polarisatierichting van licht hoeft te geven, zeggen de testen van Wollin et al. nog niets over het al of niet abiotisch gesynthetiseerd zijn van de door hen gevonden organische verbindingen.

G. Wollin and W.B.F. Ryan, Biochim. Biophys. Acta 584, 493 (1979)

II

Er bestaat, gezien de experimentele resultaten m.b.t. de depletion, geen aanwijzing voor het bestaan van BE condensatie in vloeibaar ^{4}He. Het is bovendien zeer twijfelachtig of voor het optreden van superfluïditeit BE condensatie noodzakelijk is.

D.L. Price in "The physics of liquid and solid Helium", Vol. II, ed. by K.H. Bennemann and J.B. Ketterson (John Wiley, New York, 1978), p. 711

III

Met behulp van de differentie methode kan op betrekkelijk eenvoudige wijze de invloed van de randvoorwaarden op de cholesterisch-nematische overgang nagegaan worden.

De methode van Marunaka et al., om de concentraties van organische stik-tof-verbindingen in biologisch materiaal te bepalen is nodeloos ingewikkeld. Deze methode bestaat uit een combinatie van gas chromatografie-massa fragmentografie en gas chromatografie-massa spectrometrie. Door een geschikte verdunning van het te bestuderen monster kan men m.b.v. gas chromatografie-massa spectrometrie echter even nauwkeurige resultaten verkrijgen.

T. Marunaka, Y. Umeno and Y. Minami, J.Chromatogr. 190, 107 (1980)

V

Het uitgangspunt, dat de elastische constanten van nematica berekend kunnen worden via ontwikkeling van de ééndeeltjes distributiefunctie, is onjuist.

R.G. Priest, Phys.Rev. A7, 720 (1973); A. Poniewierski and J. Stecki, Mol.Phys. 38, 1931 (1979); 41, 1451 (1980); J.P. Straley, Phys.Rev. A8, 2181 (1973)

VI

Op grond van symmetrieoverwegingen is direct in te zien dat de potentiaal

$$J(\vec{r}_{ij})(\hat{a}_i\hat{a}_j)^2$$

waarbij de eenheidsvectoren $\hat{a}_i$ en $\hat{a}_j$ de richting van de lange as van molecuul i resp. j aangeven en $J(\vec{r}_{ij})$ van de vector $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ afhangt, niet gebruikt kan worden om de lengte-breedte verhouding van de moleculen in rekening te brengen.

R.G. Priest, Mol.Cryst.Liq.Cryst. 17, 129 (1972)

VII

Verwijzingen naar "private communications" in wetenschappelijke publicaties hebben geen betekenis, uitgezonderd misschien een imponerende, en dienen daarom weggelaten te worden.

VIII

Vaak wordt vergeten dat door het bombarderen van in werking zijnde, bovengrondse kerncentrales m.b.v. "gewone" bommenwerpers met "gewone" bommen deze kerncentrales, kernwapens worden.

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